

Supporting Information for:

**Palladium-Catalyzed Oxidative Amination of Activated Olefins with
N-Alkyl Anilines for Synthesis of Tertiary (*E*)-Enamines**

Mi-Na Zhao, Xiao-Li Lian, Zhi-Hui Ren, Yao-Yu Wang, Zheng-Hui Guan*

*Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of
Education, Department of Chemistry & Materials Science, Northwest University, Xi'an
710127, P. R. China*

E-mail: guanzzhh@nwu.edu.cn

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1. General Information

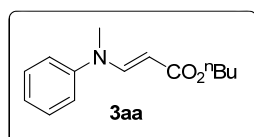
^1H NMR spectra were recorded on 400 MHz and ^{13}C NMR spectra were recorded on 100 MHz in CDCl_3 . The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. All products were further characterized by HRMS; copies of their ^1H NMR and ^{13}C NMR spectra are provided. Unless otherwise stated, all reagents and solvents were purchased from commercial suppliers and used without further purification. The *N*-alkyl anilines were prepared from the corresponding anilines according to the literature procedures.^[1]

[1] a) Y. Pen, H. Liu, M. Tang, L. Cai, V. Pike, *Chin. J. Chem.* **2009**, *27*, 1339; b) E. Byun, B. Hong, K. De Castro, M. Lim, H. Rhee, *J. Org. Chem.* **2007**, *72*, 9815; c) J. Jiao, X.-R. Zhang, N.-H. Chang, J. Wang, J.-F. Wei, X.-Y. Shi, Z.-G. Chen, *J. Org. Chem.* **2011**, *76*, 1180.

2. General Procedure for Palladium-Catalyzed Oxidative Amination of Activated Olefins with *N*-Alkyl Anilines

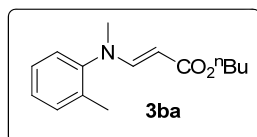
N-alkyl aniline (0.2 mmol), acrylate (0.3 mmol), PdCl_2 (5 mol%, 2.2 mg), $\text{Cu}(\text{OAc})_2$ (0.24 mmol, 43.6mg), PivOH (0.2 mmol, 20.4 mg), and CH_3CN (2 mL) was charged in a 10 mL round bottom flask. Then, the reaction mixture was stirred at 100 °C. When the reaction was completed (detected by TLC), the mixture was cooled to room temperature. The reaction was quenched with H_2O (10 mL) and extracted with EtOAc (3×10 mL) or CH_2Cl_2 (3×10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and then evaporated in vacuo. The residue was purified by column chromatography on silica gel to afford the corresponding enamine with ethyl acetate/hexanes as the eluent.

3. Characterization of compounds

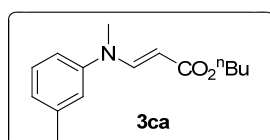


3aa: Yield: 84% (39.1 mg), colourless liquid. IR (KBr, cm^{-1}): 3066, 2958, 2671, 1737, 1694, 1622, 1499, 1459, 1343, 1263, 1159, 1034, 978, 802, 759, 696, 517. ^1H NMR (CDCl_3 , 400 MHz): δ = 7.94 (d, J = 13.2 Hz, 1 H), 7.36 (t, J = 7.6 Hz, 2 H), 7.13 (d, J = 8.0 Hz, 3 H), 4.95 (d, J = 13.2 Hz, 1 H), 4.14 (t, J = 6.4 Hz, 2 H), 3.24 (s, 3 H), 1.68-1.62 (m, 2 H), 1.44-1.38 (m, 2 H), 0.96 (t, J =

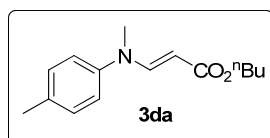
7.2 Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ = 169.3, 148.3, 146.5, 129.4, 124.0, 119.7, 90.4, 63.2, 36.5, 31.0, 19.2, 13.8. HRMS Calcd (ESI) m/z for $\text{C}_{14}\text{H}_{19}\text{NNaO}_2$: $[\text{M}+\text{Na}]^+$ 256.1308, found: 256.1303.



3ba: Yield: 92% (45.4 mg), pale yellow liquid. IR (KBr, cm^{-1}): 3097, 2957, 1692, 1620, 1495, 1456, 1334, 1255, 1157, 1100, 982, 799, 768, 728, 623. ^1H NMR (CDCl_3 , 400 MHz): δ = 7.59 (d, J = 12.8 Hz, 1 H), 7.23-7.21 (m, 3 H), 7.09-7.07 (m, 1 H), 4.83 (s, 1 H), 4.08 (m, 2 H), 3.13 (s, 3 H), 2.24 (s, 3 H), 1.63-1.59 (m, 2 H), 1.41-1.36 (m, 2 H), 0.94-0.91 (m, 3 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ = 131.4, 131.4, 63.1, 31.1, 19.2, 13.8. HRMS Calcd (ESI) m/z for $\text{C}_{15}\text{H}_{21}\text{NNaO}_2$: $[\text{M}+\text{Na}]^+$ 270.1465, found: 270.1466.

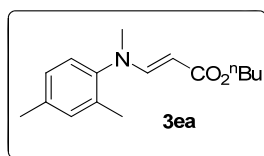


3ca: Yield: 70% (34.6 mg), colourless liquid. IR (KBr, cm^{-1}): 3074, 2954, 1698, 1616, 1499, 1458, 1335, 1254, 1159, 1099, 985, 796, 766, 727, 617. ^1H NMR (CDCl_3 , 400 MHz): δ = 7.94 (d, J = 12.8 Hz, 1 H), 7.24 (t, J = 7.6 Hz, 1 H), 6.94-6.92 (m, 3 H), 4.93 (d, J = 13.2 Hz, 1 H), 4.14 (t, J = 6.8 Hz, 2 H), 3.22 (s, 3 H), 2.36 (s, 3 H), 1.66-1.63 (m, 2 H), 1.44-1.39 (m, 2 H), 0.96 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ = 169.3, 148.4, 146.5, 139.4, 129.1, 124.9, 120.5, 116.8, 90.0, 63.2, 36.5, 31.0, 21.4, 19.2, 13.8. HRMS Calcd (ESI) m/z for $\text{C}_{15}\text{H}_{21}\text{NNaO}_2$: $[\text{M}+\text{Na}]^+$ 270.1465, found: 270.1462.

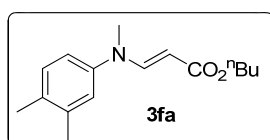


3da: Yield: 68% (33.6 mg), colourless liquid. IR (KBr, cm^{-1}): 3099, 3031, 2958, 1694, 1601, 1515, 1458, 1405, 1261, 1158, 982, 811, 737, 618, 549. ^1H NMR (CDCl_3 , 400 MHz): δ = 7.92 (d, J = 12.8 Hz, 1 H), 7.14 (d, J = 8.4 Hz, 2 H), 7.01 (d, J = 8.4 Hz, 2 H), 4.91 (d, J = 12.8 Hz, 1 H), 4.15 (t, J = 6.4 Hz, 2 H), 3.21 (s, 3 H), 2.32 (s, 3 H), 1.66-1.61 (m, 2 H), 1.42-1.38 (m, 2 H), 0.95 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ = 169.4, 148.6, 144.2, 133.8, 129.8, 119.9, 89.6, 63.2, 36.7, 31.0, 20.6, 19.2, 13.7. HRMS Calcd (ESI) m/z for $\text{C}_{15}\text{H}_{21}\text{NNaO}_2$: $[\text{M}+\text{Na}]^+$ 270.1465, found:

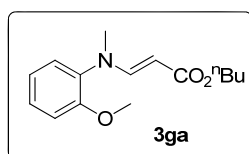
270.1457.



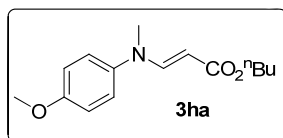
3ea: Yield: 93% (48.5 mg), colourless liquid. IR (KBr, cm^{-1}): 3128, 2925, 2855, 1692, 1621, 1404, 1257, 1144, 1104, 799, 742, 617. ^1H NMR (CDCl_3 , 400 MHz): δ = 7.54 (d, J = 10.4 Hz, 1 H), 7.03-6.93 (m, 3 H), 4.05 (s, 2 H), 3.68-3.67 (m, 1H), 3.06 (s, 3 H), 2.30 (s, 3 H), 2.11-2.09 (m, 3 H), 1.58-1.55 (m, 2 H), 1.37-1.35 (m, 2 H), 0.92-0.88 (m, 3 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ = 132.0, 63.0, 31.1, 22.7, 20.9, 19.2, 13.8. HRMS Calcd (ESI) m/z for $\text{C}_{16}\text{H}_{23}\text{NNaO}_2$: $[\text{M}+\text{Na}]^+$ 284.1621, found: 284.1618.



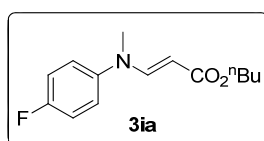
3fa: Yield: 80% (41.8 mg), colourless liquid. IR (KBr, cm^{-1}): 3125, 2958, 1694, 1601, 1506, 1453, 1403, 1332, 1265, 1155, 1112, 1028, 977, 802, 736, 617. ^1H NMR (CDCl_3 , 400 MHz): δ = 7.90 (d, J = 13.2 Hz, 1 H), 7.09 (d, J = 8.0 Hz, 1 H), 6.91 (s, 1 H), 6.86 (d, J = 8.0 Hz, 1 H), 4.88 (d, J = 13.2 Hz, 1 H), 4.13 (t, J = 6.8 Hz, 2 H), 3.20 (s, 3 H), 2.26 (s, 3 H), 2.23 (s, 3 H), 1.67-1.60 (m, 2 H), 1.44-1.38 (m, 2 H), 0.95 (t, J = 7.6 Hz, 3 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ = 169.5, 148.8, 144.6, 137.7, 132.6, 130.3, 121.4, 117.4, 89.4, 63.2, 36.8, 31.1, 19.9, 19.2, 19.0, 13.8. HRMS Calcd (ESI) m/z for $\text{C}_{16}\text{H}_{23}\text{NNaO}_2$: $[\text{M}+\text{Na}]^+$ 284.1621, found: 284.1618.



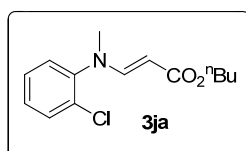
3ga: Yield: 74% (38.9 mg), pale yellow liquid. IR (KBr, cm^{-1}): 3129, 2925, 2855, 1691, 1617, 1503, 1404, 1266, 1110, 801, 748, 617. ^1H NMR (CDCl_3 , 400 MHz): δ = 7.66 (d, J = 13.2 Hz, 1 H), 7.24-7.20 (m, 1 H), 7.10-7.08 (m, 1 H), 6.96-6.93 (m, 2 H), 4.81 (s, 1 H), 4.10 (t, J = 6.8 Hz, 2 H), 3.84 (s, 3 H), 3.14 (s, 3 H), 1.63-1.60 (m, 2 H), 1.42-1.37 (m, 2 H), 0.94 (t, J = 7.6 Hz, 3 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ = 169.6, 121.0, 112.1, 63.0, 55.6, 31.1, 22.7, 19.3, 13.8. HRMS Calcd (ESI) m/z for $\text{C}_{15}\text{H}_{21}\text{NNaO}_2$: $[\text{M}+\text{Na}]^+$ 270.1465, found: 270.1466.



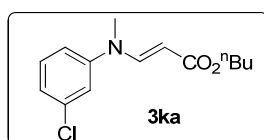
3ha: Yield: 62% (31.5 mg), pale yellow liquid. IR (KBr, cm^{-1}): 3123, 2926, 1690, 1611, 1513, 1406, 1246, 1155, 1121, 981, 825, 617. ^1H NMR (CDCl_3 , 400 MHz): δ = 7.81 (d, J = 12.8 Hz, 1 H), 7.06-7.04 (m, 2 H), 6.88-6.86 (m, 2 H), 4.84 (d, J = 12.8 Hz, 1 H), 4.11 (t, J = 6.8 Hz, 2 H), 3.79 (s, 3 H), 3.19 (s, 3 H), 1.64-1.61 (m, 2 H), 1.41-1.39 (m, 2 H), 0.94 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ = 169.4, 156.6, 149.3, 140.1, 121.9, 114.5, 88.9, 63.1, 55.4, 37.4, 31.0, 19.2, 13.7. HRMS Calcd (ESI) m/z for $\text{C}_{15}\text{H}_{22}\text{NO}_3$: $[\text{M}+\text{H}]^+$ 264.1594, found: 264.1594.



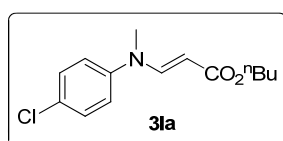
3ia: Yield: 75% (37.7 mg), colourless liquid. IR (KBr, cm^{-1}): 3111, 2959, 1693, 1620, 1510, 1403, 1336, 1228, 1159, 981, 834, 803, 617, 519. ^1H NMR (CDCl_3 , 400 MHz): δ = 7.75 (d, J = 13.2 Hz, 1 H), 7.02-6.94 (m, 4 H), 4.85 (d, J = 13.2 Hz, 1 H), 4.06-4.02 (m, 2 H), 3.14 (s, 3 H), 1.58-1.52 (m, 2 H), 1.36-1.30 (m, 2 H), 0.88-0.84 (m, 3 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ = 169.2, 159.5 (d, J_{CF} = 242.9 Hz), 148.6, 142.9, 121.8 (d, J_{CF} = 8.3 Hz), 116.1 (d, J_{CF} = 22.7 Hz), 90.3, 63.3, 37.1, 31.0, 19.2, 13.7. HRMS Calcd (ESI) m/z for $\text{C}_{14}\text{H}_{18}\text{FNNaO}_2$: $[\text{M}+\text{Na}]^+$ 274.1214, found: 274.1212.



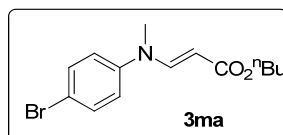
3ja: Yield: 78% (41.7 mg), colourless liquid. ^1H NMR (CDCl_3 , 400 MHz): δ = 7.88 (d, J = 12.8 Hz, 1 H), 7.27-7.23 (m, 1 H), 7.11 (d, J = 8.0 Hz, 1 H), 7.09-7.05 (m, 1 H), 7.01-6.99 (m, 1 H), 4.99 (d, J = 13.2 Hz, 1 H), 4.13 (t, J = 6.8 Hz, 2 H), 3.21 (s, 3 H), 1.66-1.60 (m, 2 H), 1.43-1.38 (m, 2 H), 0.95 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ = 169.2, 130.8, 127.9, 89.0, 63.2, 31.0, 19.2, 13.8. HRMS Calcd (ESI) m/z for $\text{C}_{14}\text{H}_{18}\text{ClNNaO}_2$: $[\text{M}+\text{Na}]^+$ 290.0918, found: 290.0923.



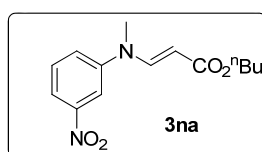
3ka: Yield: 70% (37.4 mg), pale yellow liquid. IR (KBr, cm^{-1}): 3096, 2958, 2870, 1696, 1622, 1584, 1485, 1332, 1265, 1162, 1034, 999, 806, 777, 687, 615. ^1H NMR (CDCl_3 , 400 MHz): δ = 7.89 (d, J = 13.2 Hz, 1 H), 7.29-7.25 (m, 1 H), 7.11-7.00 (m, 3 H), 5.00 (d, J = 13.2 Hz, 1 H), 4.14 (t, J = 6.8 Hz, 2 H), 3.22 (s, 3 H), 1.68-1.61 (m, 2 H), 1.44-1.37 (m, 2 H), 0.96 (t, J = 7.6 Hz, 3 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ = 169.0, 147.5, 147.4, 135.1, 130.4, 123.8, 119.6, 117.4, 91.9, 63.4, 36.2, 31.0, 19.2, 13.8. HRMS Calcd (ESI) m/z for $\text{C}_{14}\text{H}_{18}\text{ClNNaO}_2$: $[\text{M}+\text{Na}]^+$ 290.0918, found: 290.0920.



3la: Yield: 87% (46.5 mg), colourless liquid. IR (KBr, cm^{-1}): 3100, 2925, 2856, 1696, 1620, 1586, 1496, 1458, 1403, 1333, 1263, 1160, 1122, 1069, 980, 823, 618, 520. ^1H NMR (CDCl_3 , 400 MHz): δ = 7.87 (d, J = 13.2 Hz, 1 H), 7.31 (d, J = 8.8 Hz, 2 H), 7.06 (d, J = 8.8 Hz, 2 H), 4.97 (d, J = 13.2 Hz, 1 H), 4.14 (t, J = 6.8 Hz, 2 H), 3.22 (s, 3 H), 1.66-1.61 (m, 2 H), 1.42-1.40 (m, 2 H), 0.96 (t, J = 7.6 Hz, 3 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ = 169.1, 147.8, 145.1, 129.4, 120.9, 91.3, 63.4, 36.6, 31.0, 19.2, 13.8. HRMS Calcd (ESI) m/z for $\text{C}_{14}\text{H}_{18}\text{ClNNaO}_2$: $[\text{M}+\text{Na}]^+$ 290.0918, found: 290.0924.

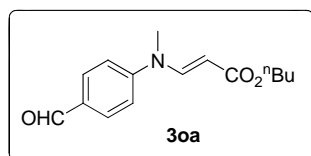


3ma: Yield: 84% (52.2 mg), pale yellow liquid. IR (KBr, cm^{-1}): 3096, 2958, 2871, 1693, 1617, 1582, 1494, 1460, 1332, 1264, 1161, 1069, 979, 808, 758, 619, 516. ^1H NMR (CDCl_3 , 400 MHz): δ = 7.85 (d, J = 13.2 Hz, 1 H), 7.43 (d, J = 8.4 Hz, 2 H), 6.98 (d, J = 8.4 Hz, 2 H), 4.96 (d, J = 13.2 Hz, 1 H), 4.12 (t, J = 6.8 Hz, 2 H), 3.20 (s, 3 H), 1.65-1.59 (m, 2 H), 1.42-1.37 (m, 2 H), 0.94 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ = 169.0, 147.6, 145.5, 132.3, 121.1, 116.8, 91.4, 63.4, 36.4, 31.0, 19.2, 13.7. HRMS Calcd (ESI) m/z for $\text{C}_{14}\text{H}_{19}\text{BrNO}_2$: $[\text{M}+\text{H}]^+$ 312.0594, found: 312.0588.

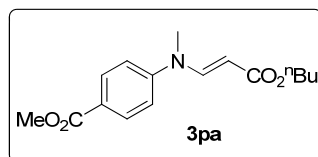


3na: Yield: 70% (38.9 mg), yellow liquid. IR (KBr, cm^{-1}): 3099, 2958, 2928, 2868, 1697, 1605,

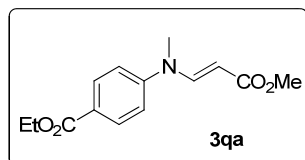
1531, 1488, 1461, 1348, 1265, 1165, 1130, 1033, 884, 803, 738, 679, 613. ^1H NMR (CDCl_3 , 400 MHz): δ = 7.97-7.93 (m, 3 H), 7.56-7.46 (m, 2 H), 5.12 (d, J = 13.2 Hz, 1 H), 4.16 (t, J = 6.8 Hz, 1 H), 3.32 (s, 3 H), 1.69-1.62 (m, 2 H), 1.45-1.39 (m, 2 H), 0.97 (t, J = 7.6 Hz, 3 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ = 168.5, 148.9, 147.1, 146.4, 130.2, 124.4, 118.0, 113.4, 93.6, 63.5, 36.0, 30.9, 19.1, 13.7. HRMS Calcd (ESI) m/z for $\text{C}_{14}\text{H}_{18}\text{N}_2\text{NaO}_4$: $[\text{M}+\text{Na}]^+$ 301.1159, found: 301.1160.



3oa: Yield: 77% (40.2 mg), white liquid. ^1H NMR (CDCl_3 , 400 MHz): δ = 8.01 (d, J = 13.2 Hz, 1 H), 7.84 (d, J = 8.0 Hz, 2 H), 7.22 (d, J = 8.4 Hz, 2 H), 5.13 (d, J = 13.2 Hz, 1 H), 4.13 (t, J = 6.4 Hz, 2 H), 3.27 (s, 3 H), 1.64-1.61 (m, 2 H), 1.42-1.36 (m, 2 H), 0.93 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ = 190.6, 168.6, 150.7, 145.9, 131.3, 131.3, 118.0, 94.2, 63.6, 35.5, 30.8, 19.1, 13.7. HRMS Calcd (ESI) m/z for $\text{C}_{15}\text{H}_{19}\text{NNaO}_3$: $[\text{M}+\text{Na}]^+$ 284.1257, found: 284.1261.

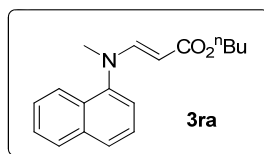


3pa: Yield: 84% (48.9 mg), white solid, mp 62-64 °C. IR (KBr, cm^{-1}): 3110, 2958, 1699, 1592, 1512, 1404, 1265, 1115, 975, 830, 768, 617. ^1H NMR (CDCl_3 , 400 MHz): δ = 8.02-7.99 (m, 3 H), 7.14 (d, J = 8.4 Hz, 2 H), 5.08 (d, J = 13.2 Hz, 1 H), 4.14 (t, J = 6.8 Hz, 2 H), 3.89 (s, 3 H), 3.26 (s, 3 H), 1.66-1.62 (m, 2 H), 1.43-1.38 (m, 2 H), 0.95 (t, J = 6.8 Hz, 3 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ = 168.8, 166.4, 149.7, 146.5, 131.1, 124.8, 117.8, 93.1, 63.5, 52.0, 35.7, 30.9, 19.2, 13.8. HRMS Calcd (ESI) m/z for $\text{C}_{16}\text{H}_{21}\text{NNaO}_4$: $[\text{M}+\text{Na}]^+$ 314.1363, found: 314.1366.

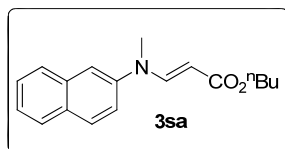


3qa: Yield: 76% (46.4 mg), pale yellow solid, mp 67-69 °C. IR (KBr, cm^{-1}): 3144, 1706, 1624, 1588, 1513, 1404, 1263, 1170, 1124, 1023, 977, 844, 795, 766, 697, 617. ^1H NMR (CDCl_3 , 400 MHz): δ = 8.04-8.01 (m, 3 H), 7.16 (d, J = 8.8 Hz, 2 H), 5.08 (d, J = 13.2 Hz, 1 H), 4.39-4.34 (m, 2 H), 3.73 (s, 3 H), 3.27 (s, 3 H), 1.40 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ = 169.1, 165.9, 149.6, 146.8, 131.1, 125.3, 117.9, 92.5, 60.9, 51.0, 35.7, 14.3. HRMS Calcd (ESI) m/z for

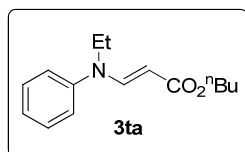
C₁₄H₁₇NNaO₄: [M+Na]⁺ 286.1050, found: 286.1051.



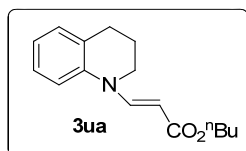
3ra: Yield: 60% (34.0 mg), pale yellow liquid. IR (KBr, cm⁻¹): 3121, 2926, 2859, 1693, 1615, 1508, 1459, 1401, 1324, 1268, 1157, 1133, 1078, 975, 800, 776, 616. ¹H NMR (CDCl₃, 400 MHz): δ = 7.90 (d, *J* = 8.4 Hz, 1 H), 7.81-7.77 (m, 3 H), 7.66-7.51 (m, 2 H), 7.48-7.44 (m, 1 H), 7.30-7.26 (m, 1 H), 4.97 (s, 1 H), 4.09 (s, 2 H), 3.32 (s, 3 H), 1.61 (s, 2 H), 1.39-1.37 (m, 2 H), 0.93 (t, *J* = 7.2 Hz, 3 H); ¹³C NMR (CDCl₃, 100 MHz): δ = 169.4, 134.7, 128.5, 126.9, 126.5, 125.6, 122.8, 114.5, 88.3, 63.1, 31.0, 19.2, 13.8. HRMS Calcd (ESI) *m/z* for C₁₈H₂₁NNaO₂: [M+Na]⁺ 306.1465, found: 306.1463.



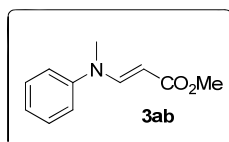
3sa: Yield: 45% (25.5 mg), pale yellow liquid. IR (KBr, cm⁻¹): 3113, 2958, 1692, 1604, 1508, 1405, 1348, 1261, 1227, 1161, 1110, 977, 801, 751, 618. ¹H NMR (CDCl₃, 400 MHz): δ = 8.09 (d, *J* = 13.2 Hz, 1 H), 7.85-7.77 (m, 3 H), 7.52-7.35 (m, 4 H), 5.04 (d, *J* = 13.2 Hz, 1 H), 4.18 (t, *J* = 6.4 Hz, 2 H), 3.35 (s, 3 H), 1.70-1.66 (m, 2 H), 1.47-1.42 (m, 2 H), 0.98 (t, *J* = 7.2 Hz, 3 H); ¹³C NMR (CDCl₃, 100 MHz): δ = 169.3, 148.4, 143.9, 133.8, 130.3, 129.4, 127.6, 127.3, 126.9, 125.2, 119.5, 116.4, 90.9, 63.3, 36.6, 31.0, 19.2, 13.8. HRMS Calcd (ESI) *m/z* for C₁₈H₂₁NNaO₂: [M+Na]⁺ 306.1465, found: 306.1459.



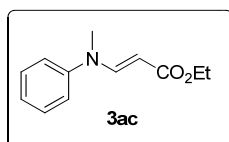
3ta: Yield: 72% (35.6 mg), colourless liquid. ¹H NMR (CDCl₃, 400 MHz): δ = 7.81 (d, *J* = 13.6 Hz, 1 H), 7.34-7.30 (m, 2 H), 7.12-7.10 (m, 3 H), 4.92 (d, *J* = 13.6 Hz, 1 H), 4.10 (t, *J* = 6.4 Hz, 2 H), 3.70-3.66 (m, 2H), 1.63-1.59 (m, 2 H), 1.41-1.35 (m, 2 H), 1.24-1.21 (m, 3 H), 0.93 (t, *J* = 7.2 Hz, 3 H); ¹³C NMR (CDCl₃, 100 MHz): δ = 169.4, 147.3, 145.1, 129.3, 124.4, 120.6, 89.5, 63.1, 30.9, 29.5, 19.1, 13.7, 11.7. HRMS Calcd (ESI) *m/z* for C₁₅H₂₁NNaO₂: [M+Na]⁺ 270.1465, found: 270.1466.



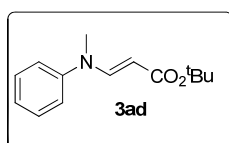
3ua: Yield: 55% (28.5 mg), pale yellow liquid. IR (KBr, cm^{-1}): 3117, 2956, 2870, 1694, 1613, 1579, 1497, 1458, 1402, 1332, 1246, 1151, 1071, 970, 803, 753, 618. ^1H NMR (CDCl_3 , 400 MHz): δ = 8.18 (d, J = 13.2 Hz, 1 H), 7.22-7.18 (m, 1 H), 7.13 (d, J = 8.0 Hz, 1 H), 7.07 (d, J = 7.2 Hz, 1 H), 6.96-6.93 (m, 1 H), 5.03 (d, J = 13.2 Hz, 1 H), 4.15 (t, J = 6.8 Hz, 2 H), 3.47 (t, J = 6.4 Hz, 2 H), 2.71 (t, J = 5.6 Hz, 2 H), 2.04-1.99 (m, 2 H), 1.69-1.62 (m, 2 H), 1.45-1.39 (m, 2 H), 0.96 (t, J = 7.6 Hz, 3 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ = 169.3, 145.5, 140.2, 128.7, 128.1, 127.6, 122.2, 115.8, 90.6, 63.3, 45.8, 31.0, 27.3, 22.3, 19.2, 13.8. HRMS Calcd (ESI) m/z for $\text{C}_{16}\text{H}_{21}\text{NNaO}_2$: $[\text{M}+\text{Na}]^+$ 282.1465, found: 282.1470.



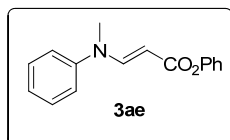
3ab: Yield: 75% (28.5 mg), pale yellow liquid. IR (KBr, cm^{-1}): 3100, 2950, 1737, 1695, 1621, 1499, 1436, 1344, 1262, 1162, 1040, 978, 802, 760, 696, 618. ^1H NMR (CDCl_3 , 400 MHz): δ = 7.86 (d, J = 13.2 Hz, 1 H), 7.28-7.24 (m, 2 H), 7.05-7.01 (m, 3 H), 4.86 (d, J = 12.8 Hz, 1 H), 3.62 (s, 3 H), 3.14 (s, 3 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ = 169.5, 148.5, 146.4, 129.4, 124.1, 119.7, 89.9, 50.8, 36.4. HRMS Calcd (ESI) m/z for $\text{C}_{11}\text{H}_{13}\text{NNaO}_2$: $[\text{M}+\text{Na}]^+$ 214.0838, found: 214.0836.



3ac: Yield: 76% (28.5 mg), pale yellow liquid. IR (KBr, cm^{-1}): 3065, 2980, 1735, 1693, 1621, 1499, 1349, 1262, 1161, 1123, 1046, 978, 802, 760, 697, 619. ^1H NMR (CDCl_3 , 400 MHz): δ = 7.94 (d, J = 13.2 Hz, 1 H), 7.36-7.32 (m, 2 H), 7.13-7.11 (m, 3 H), 4.94 (d, J = 13.2 Hz, 1 H), 4.20-4.14 (m, 2 H), 3.23 (s, 3 H), 1.30-1.25 (m, 3 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ = 169.1, 148.3, 146.5, 129.3, 124.0, 119.7, 90.3, 59.2, 36.4, 14.5. HRMS Calcd (ESI) m/z for $\text{C}_{12}\text{H}_{15}\text{NNaO}_2$: $[\text{M}+\text{Na}]^+$ 228.0995, found: 228.0992.

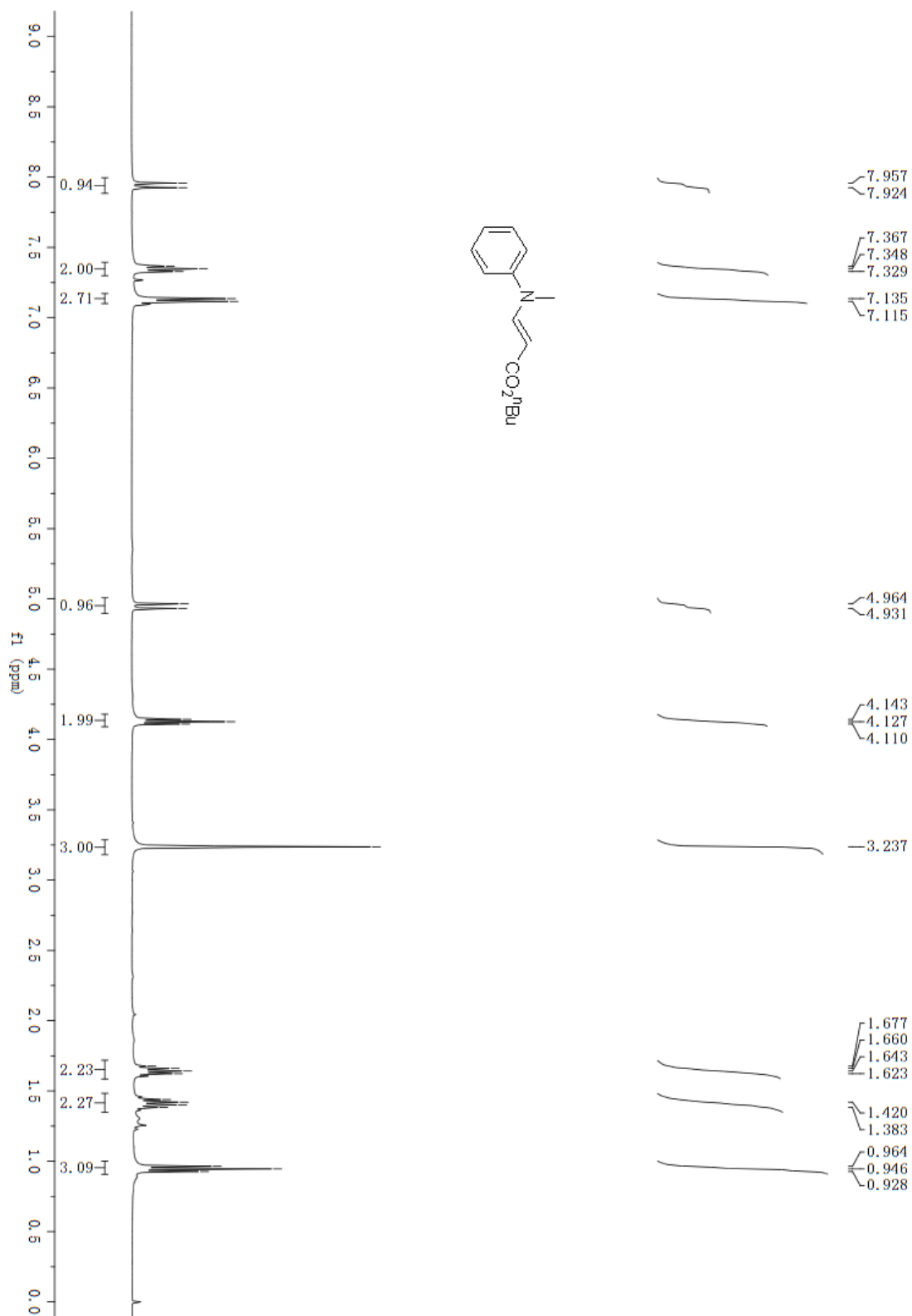
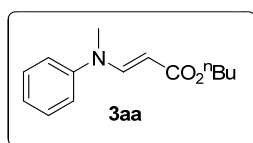


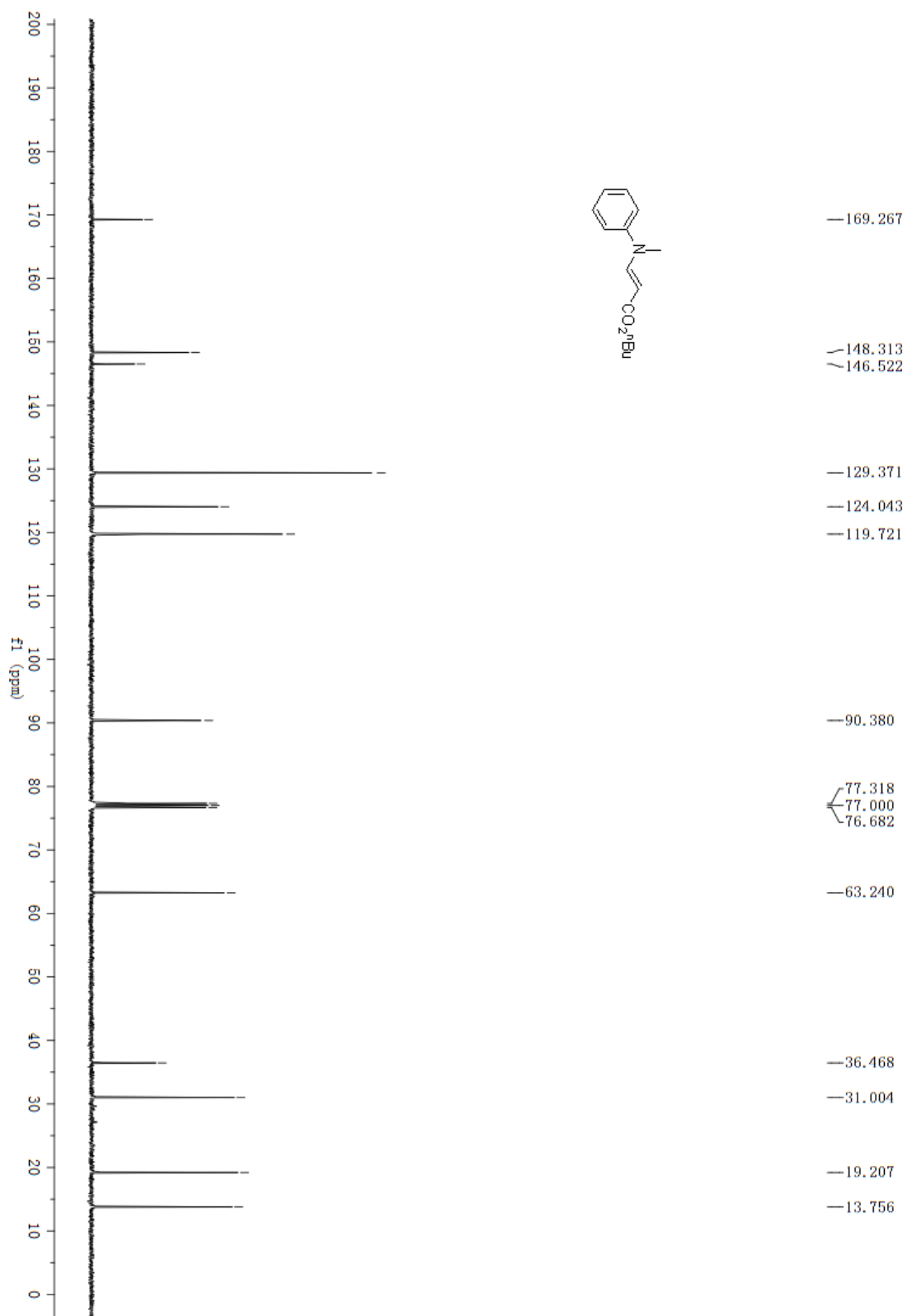
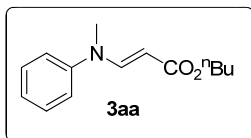
3ad: Yield: 60% (28.5 mg), pale yellow liquid. IR (KBr, cm^{-1}): 3125, 2974, 2929, 1691, 1620, 1589, 1498, 1401, 1264, 1150, 1119, 1005, 804, 757, 695, 617. ^1H NMR (CDCl_3 , 400 MHz): δ = 7.88 (d, J = 13.2 Hz, 1 H), 7.35-7.32 (m, 2 H), 7.13-7.08 (m, 3 H), 4.90 (d, J = 13.2 Hz, 1 H), 3.22 (s, 3 H), 1.50 (s, 9 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ = 168.8, 147.8, 146.7, 129.4, 123.9, 119.6, 92.3, 78.8, 36.4, 28.5. HRMS Calcd (ESI) m/z for $\text{C}_{14}\text{H}_{19}\text{NNaO}_2$: $[\text{M}+\text{Na}]^+$ 256.1308, found: 256.1303.

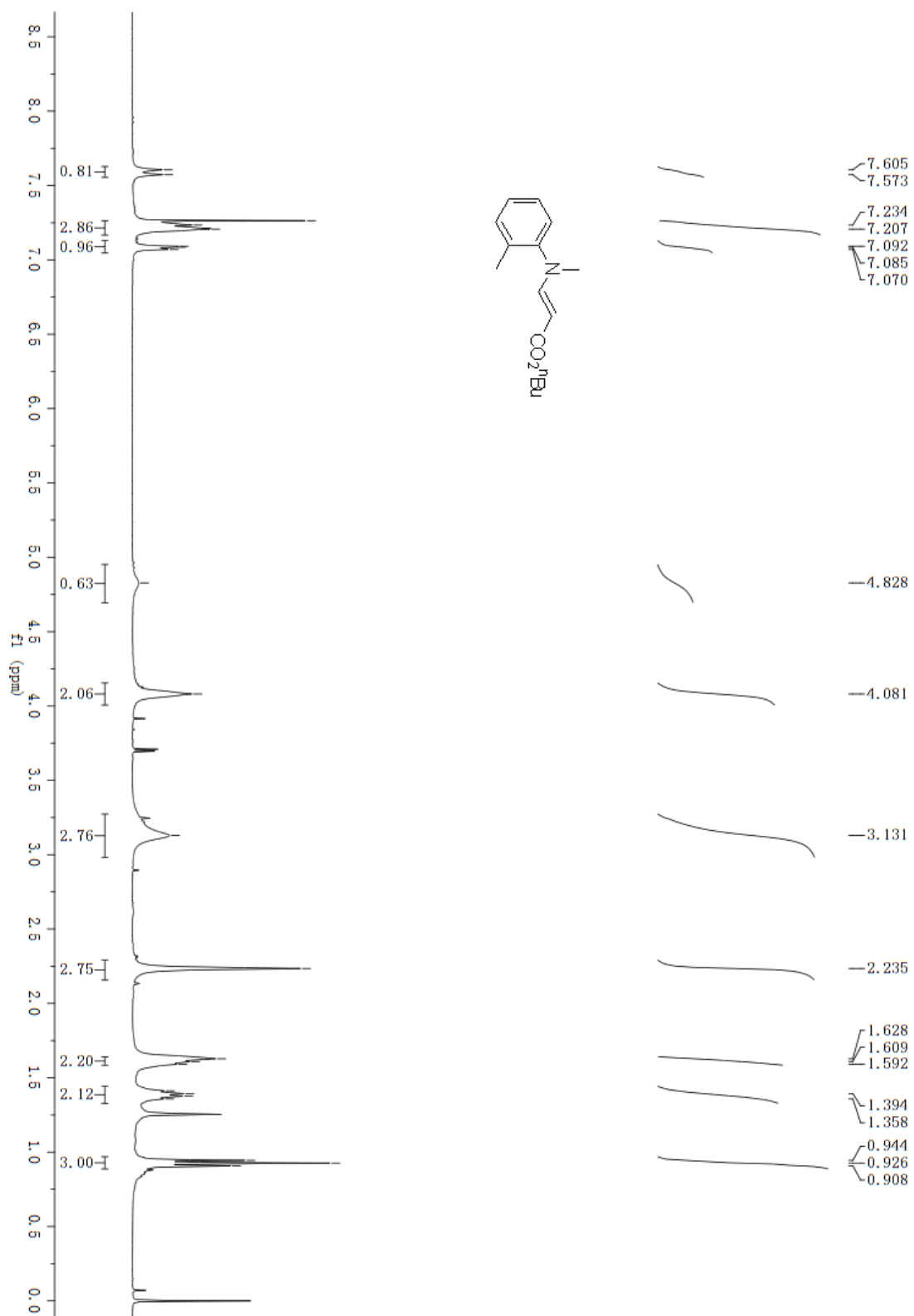
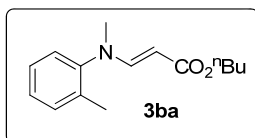


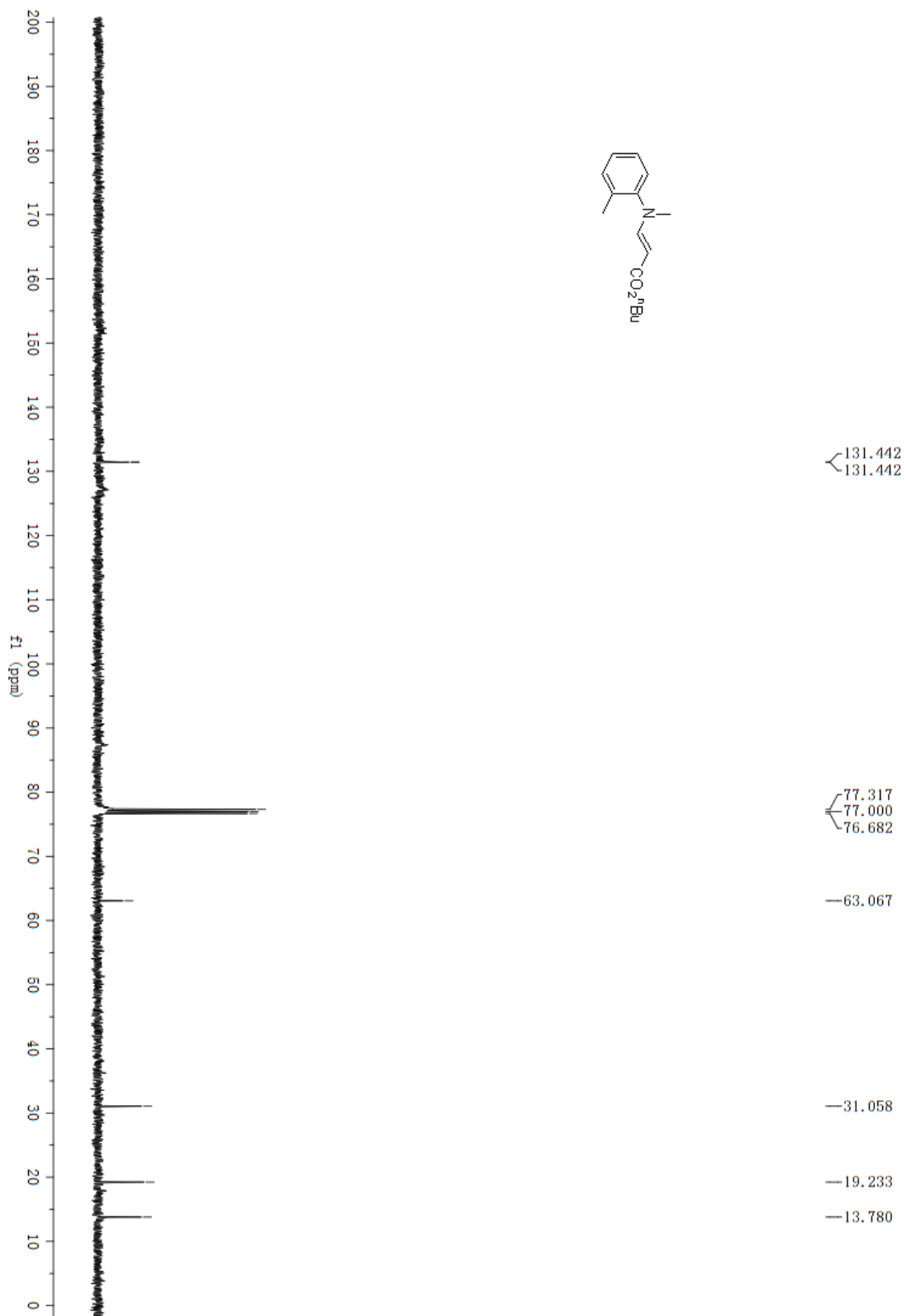
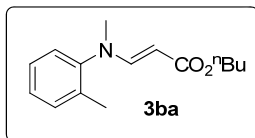
3ae: Yield: 84% (28.5 mg), pale yellow liquid. IR (KBr, cm^{-1}): 3114, 2925, 1704, 1621, 1584, 1492, 1403, 1345, 1258, 1195, 1116, 1029, 979, 817, 788, 758, 693, 618, 532. ^1H NMR (CDCl_3 , 400 MHz): δ = 8.10 (d, J = 13.2 Hz, 1 H), 7.40-7.36 (m, 4 H), 7.22-7.14 (m, 6 H), 5.13 (d, J = 13.2 Hz, 1 H), 3.32 (s, 3 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ = 167.5, 151.3, 150.0, 146.3, 129.5, 129.2, 125.0, 124.6, 121.9, 120.1, 89.1, 36.9. HRMS Calcd (ESI) m/z for $\text{C}_{16}\text{H}_{15}\text{NNaO}_2$: $[\text{M}+\text{Na}]^+$ 276.0995, found: 276.1002.

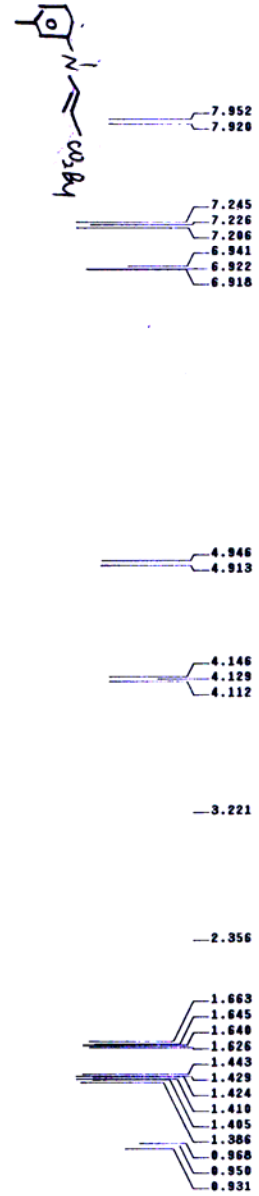
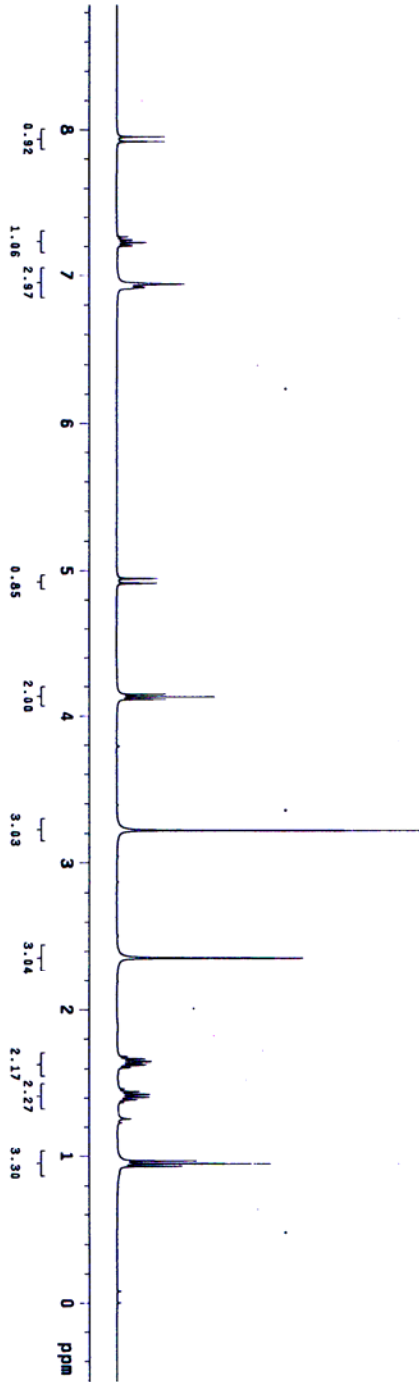
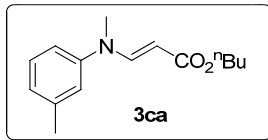
4. Copies of ^1H and ^{13}C NMR spectra

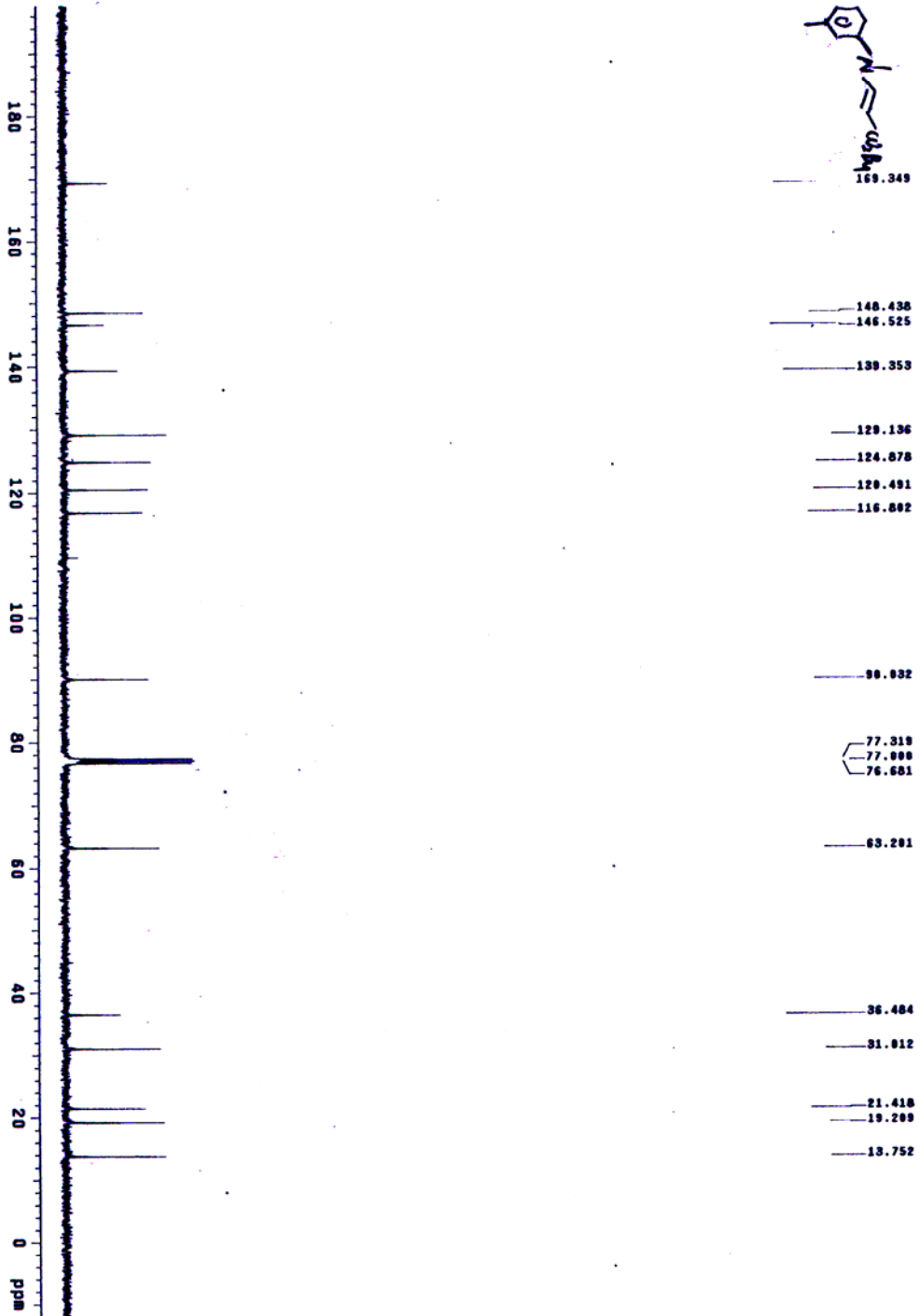
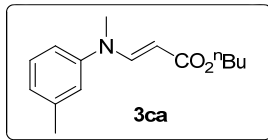


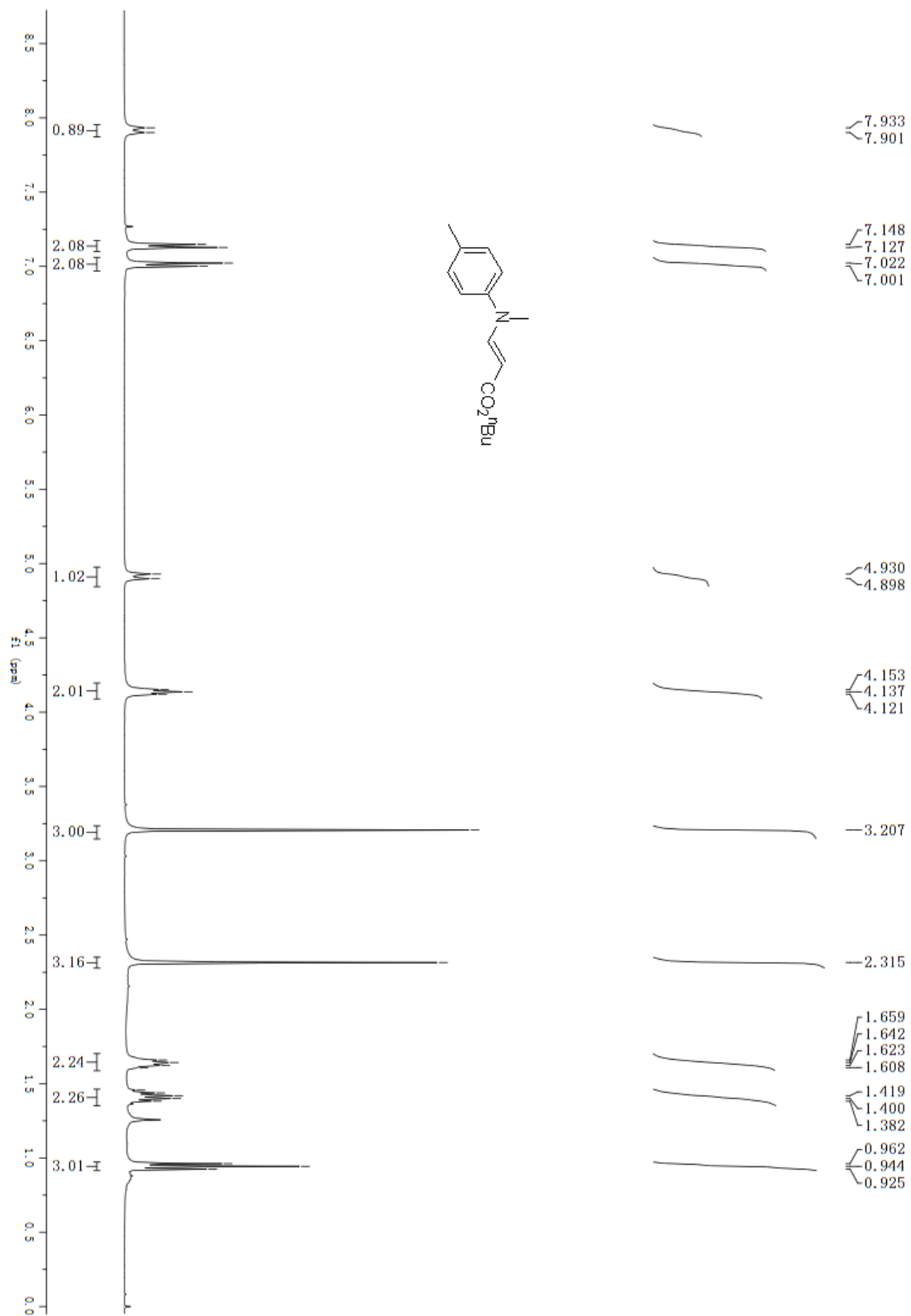
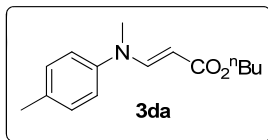


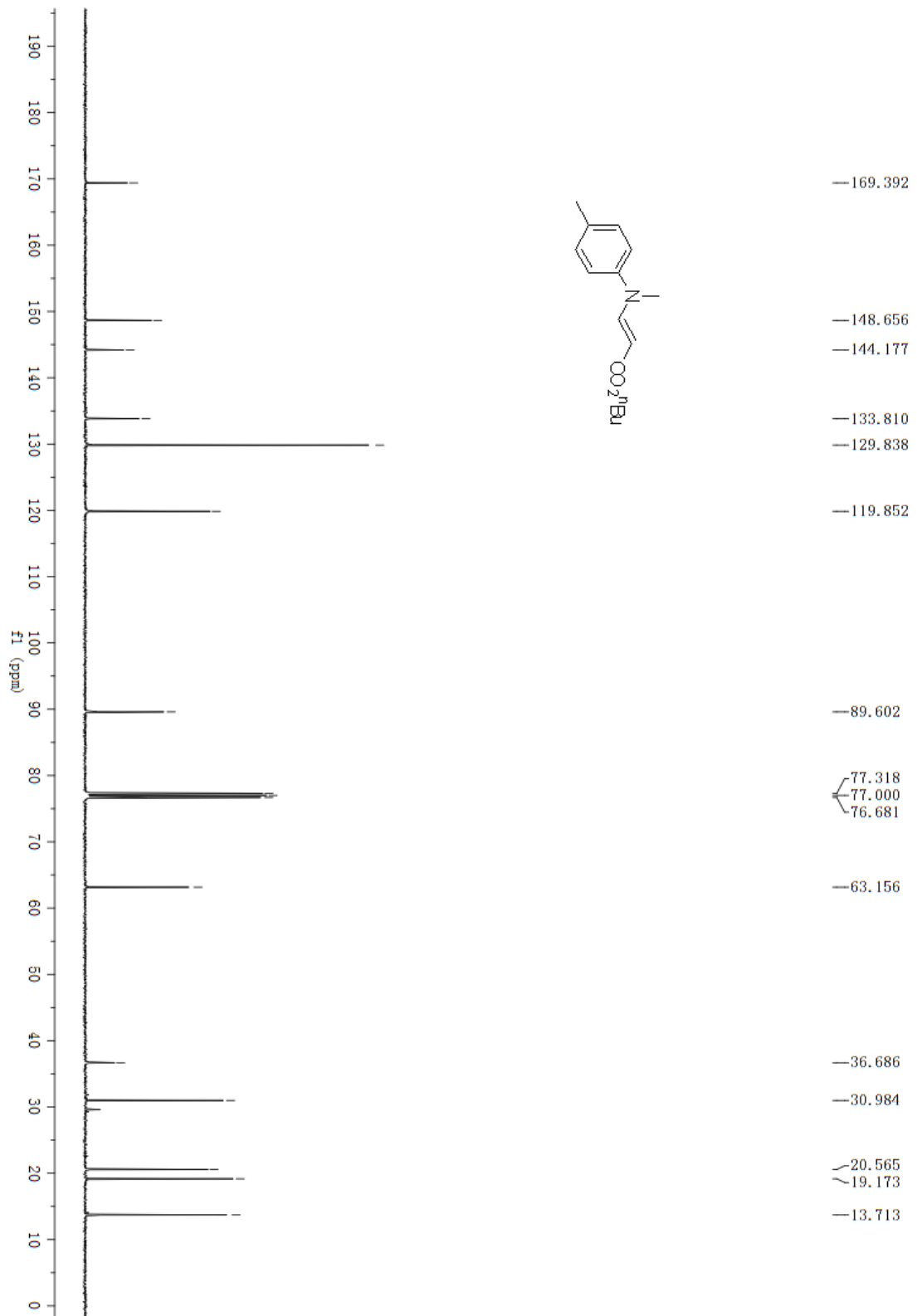
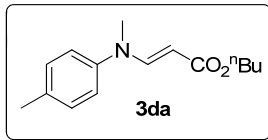


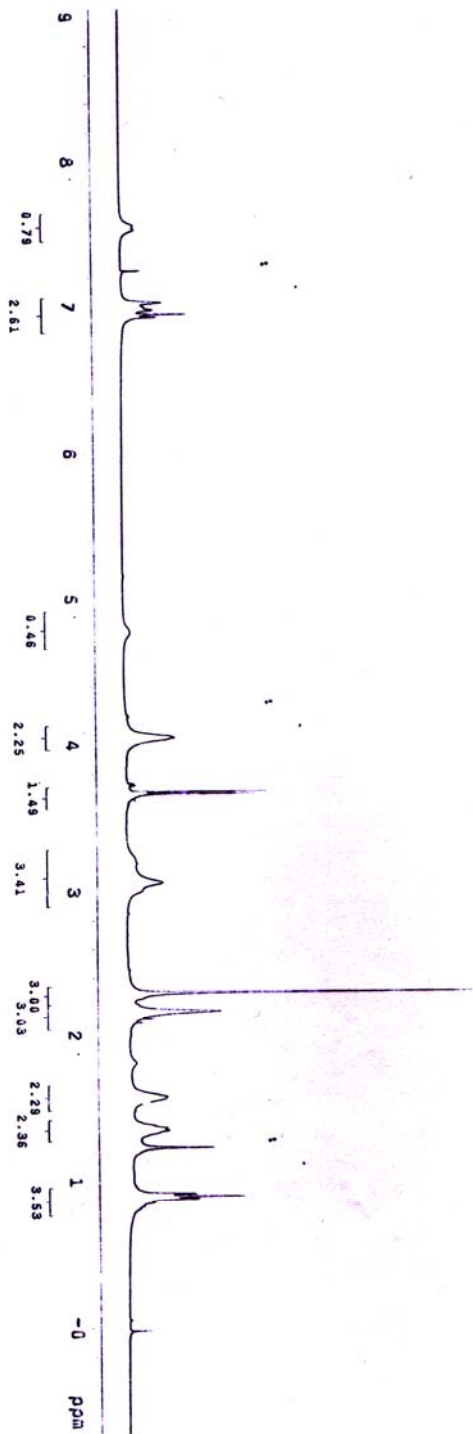
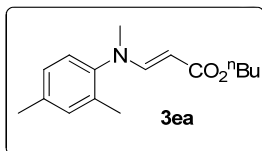


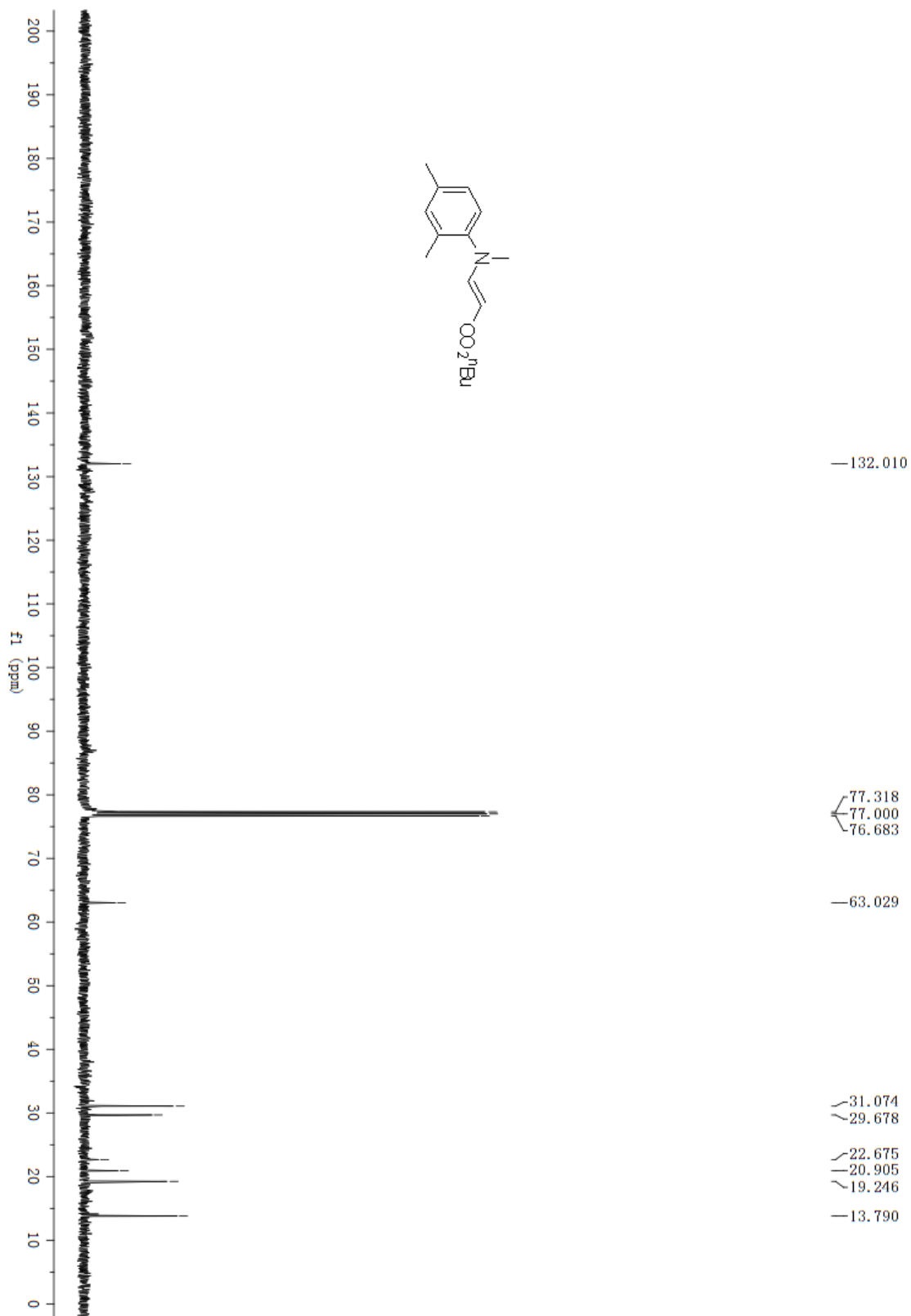
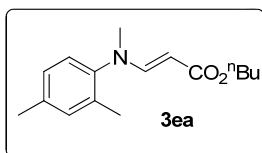


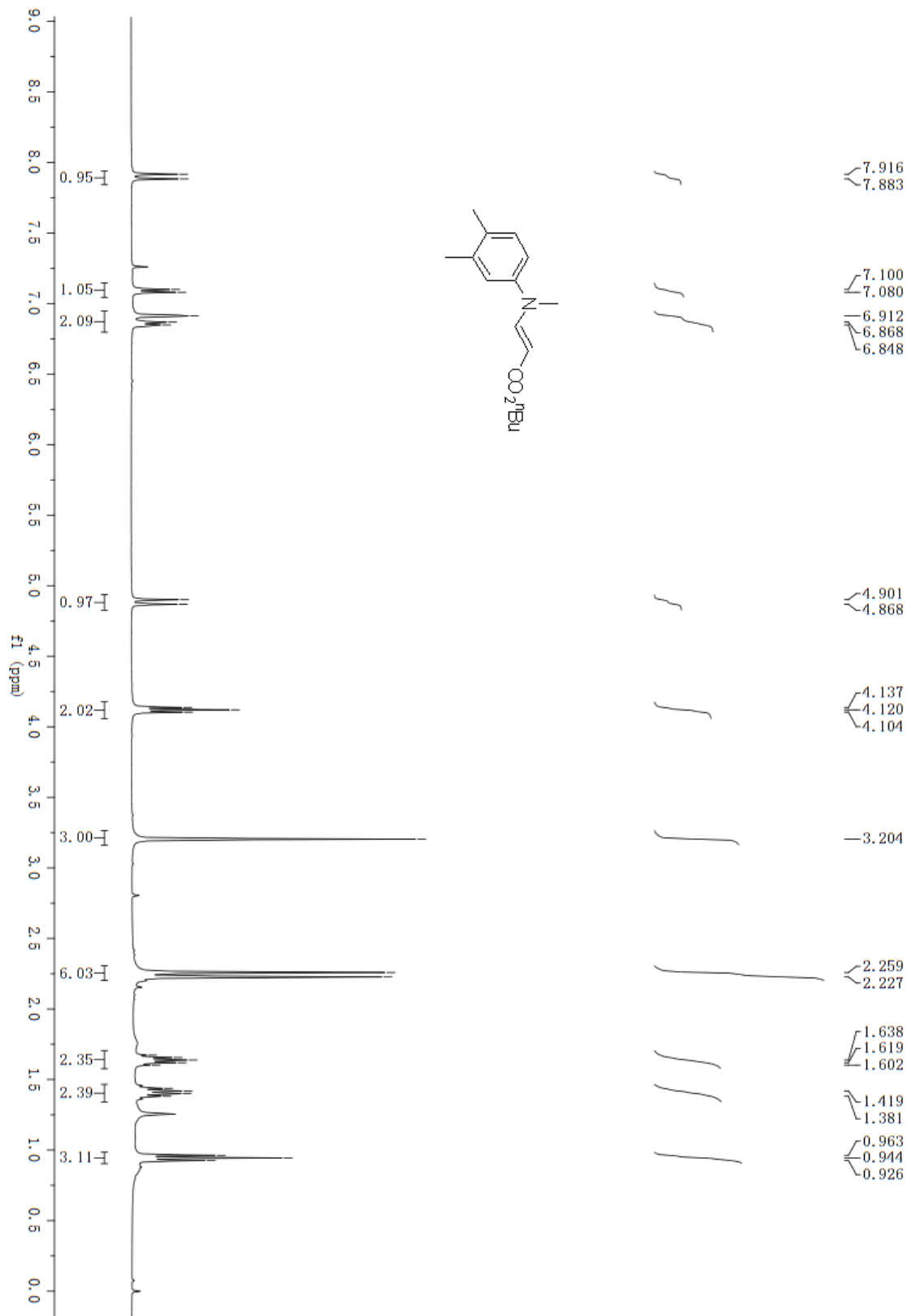
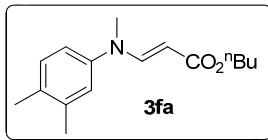


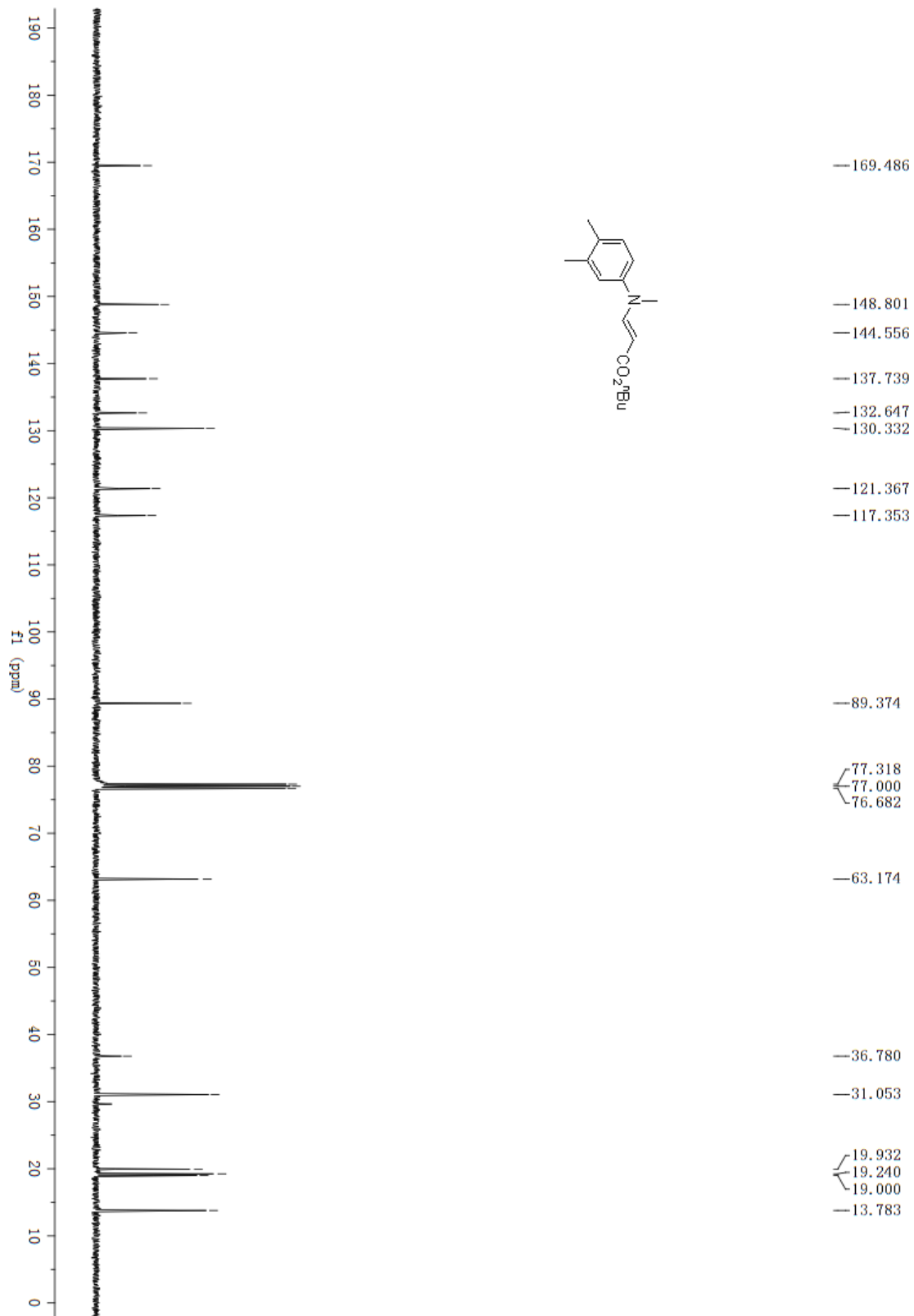
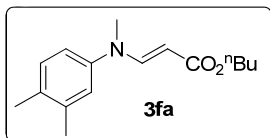


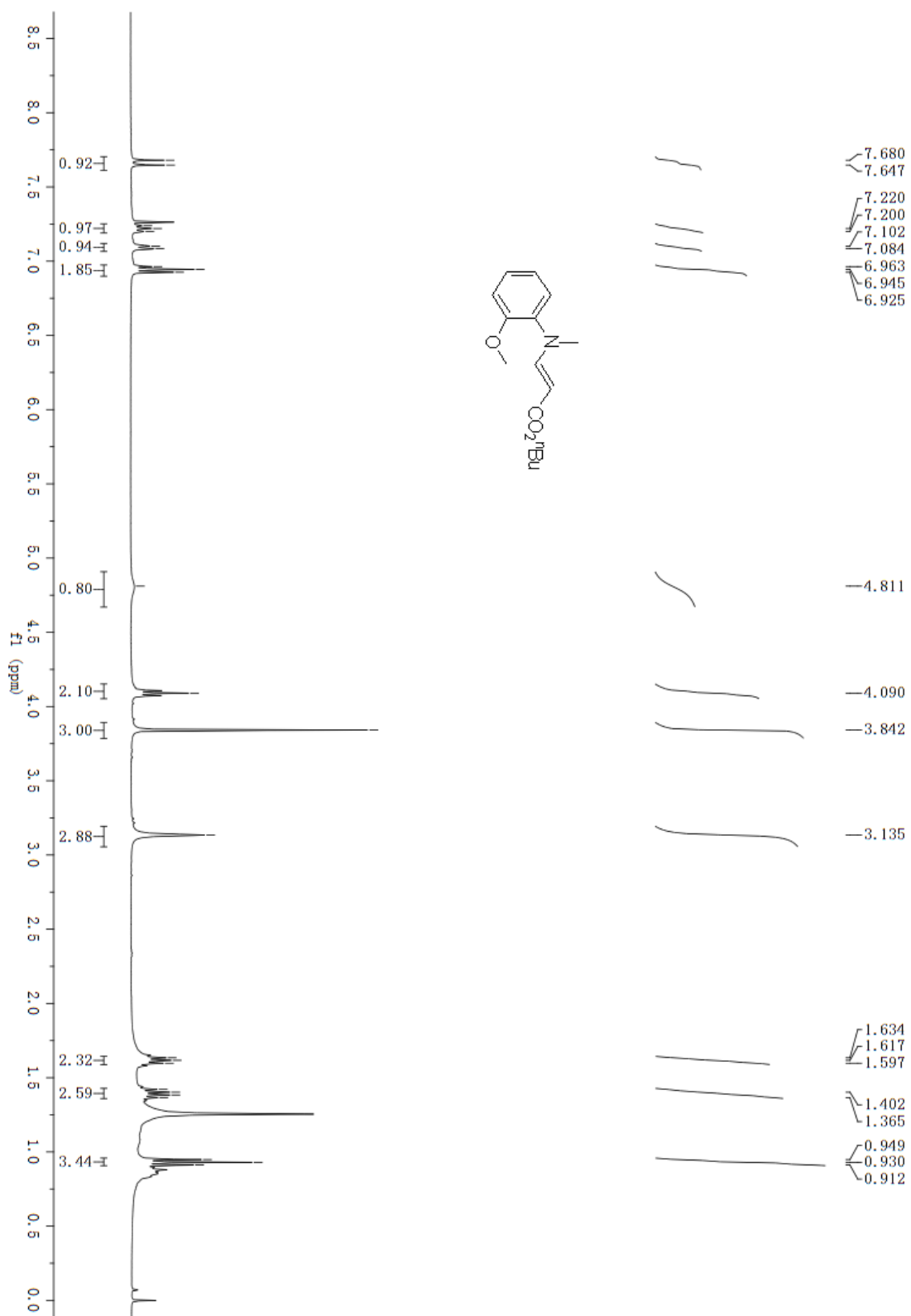
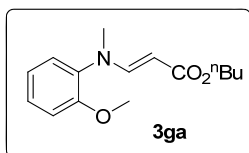


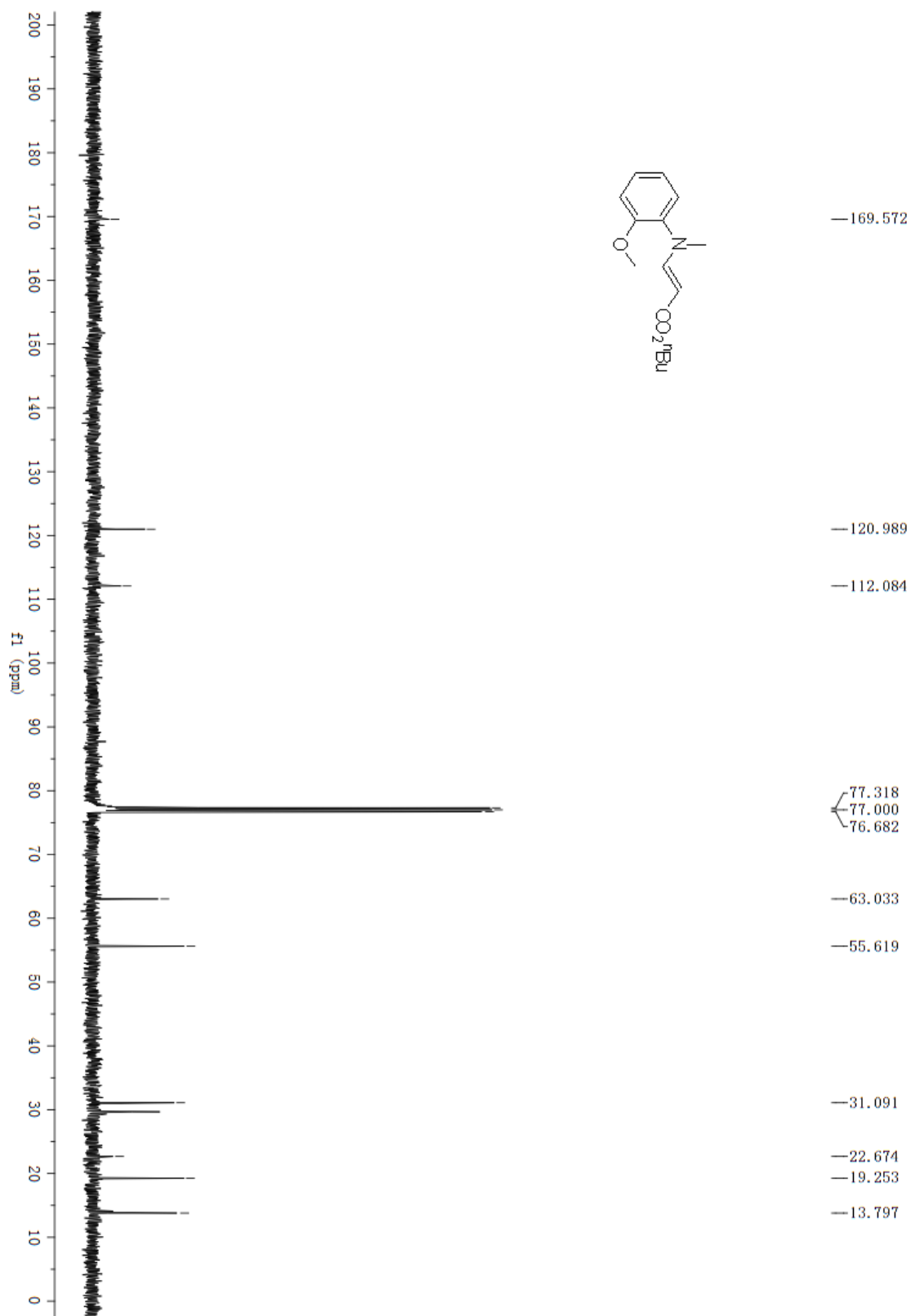
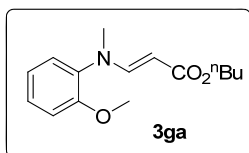


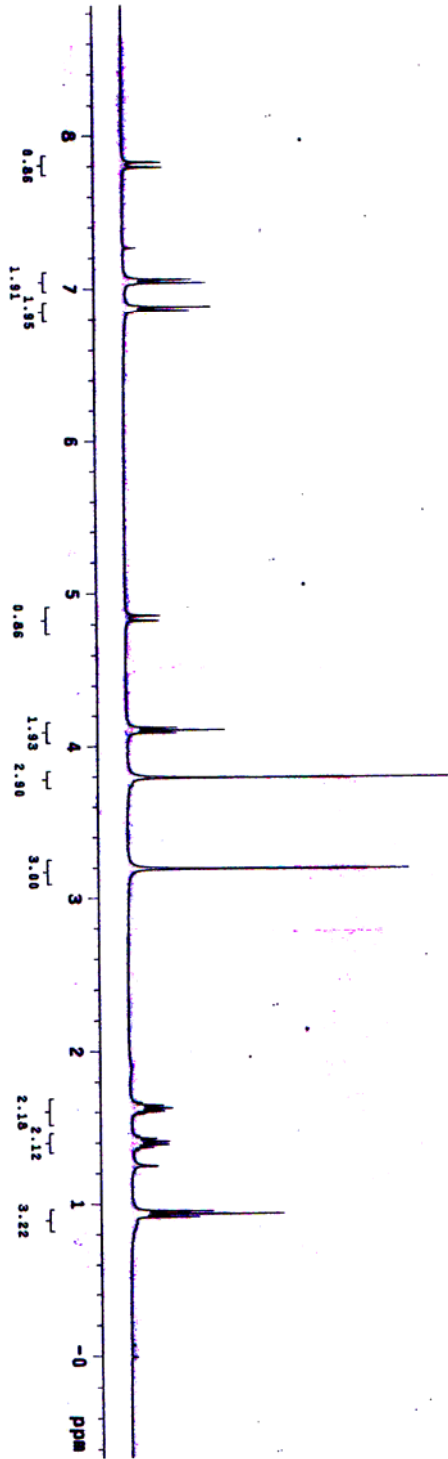
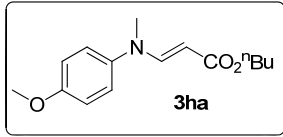


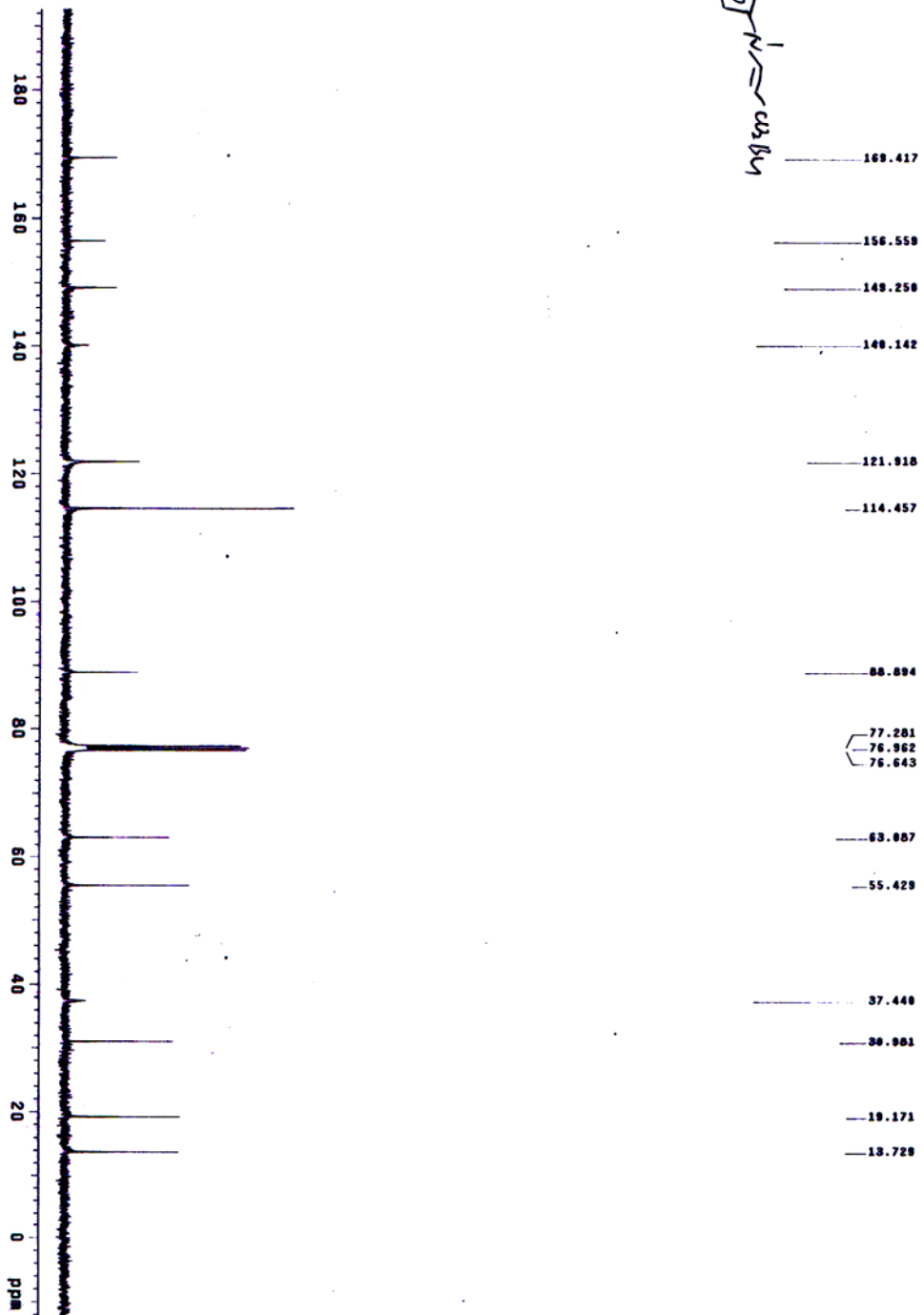
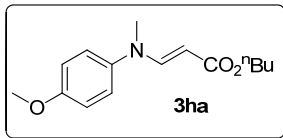


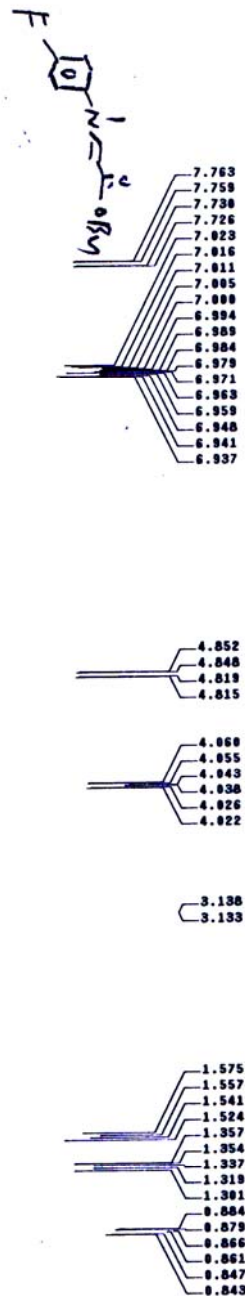
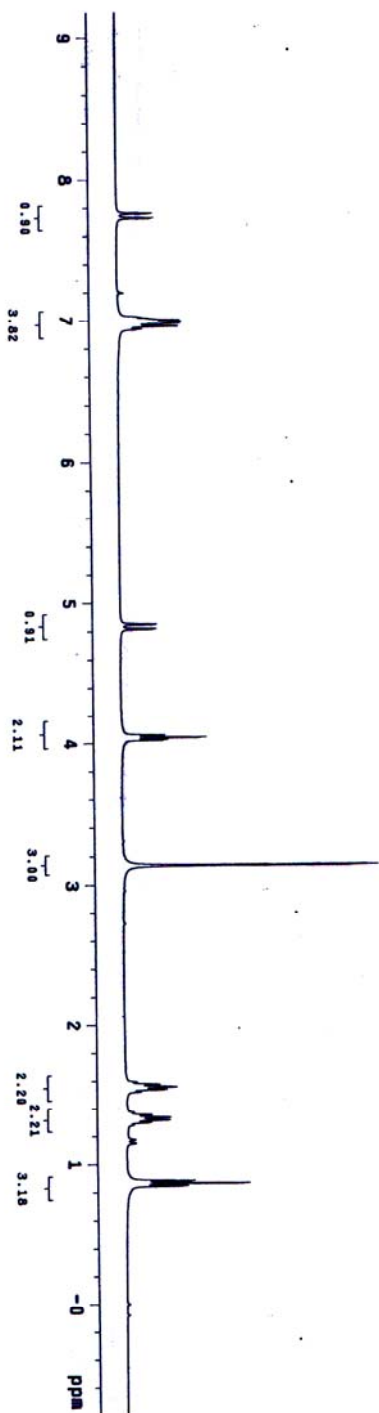
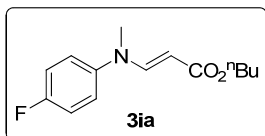


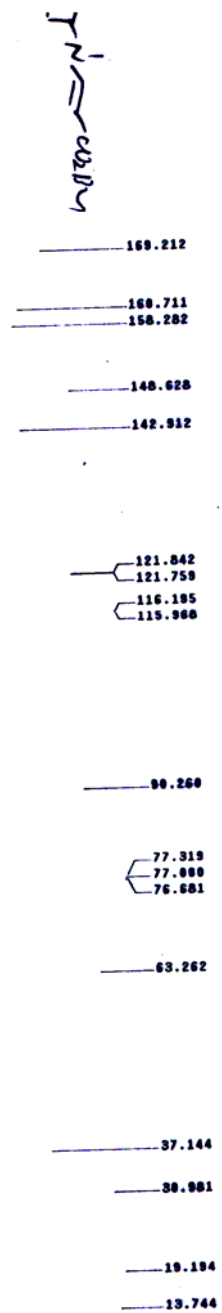
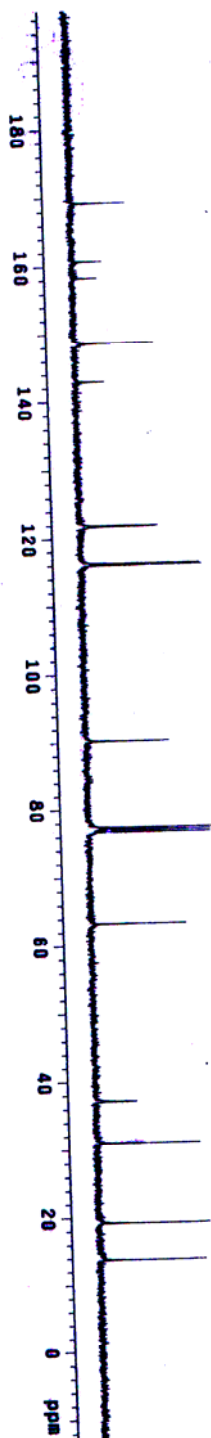
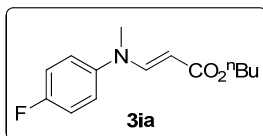


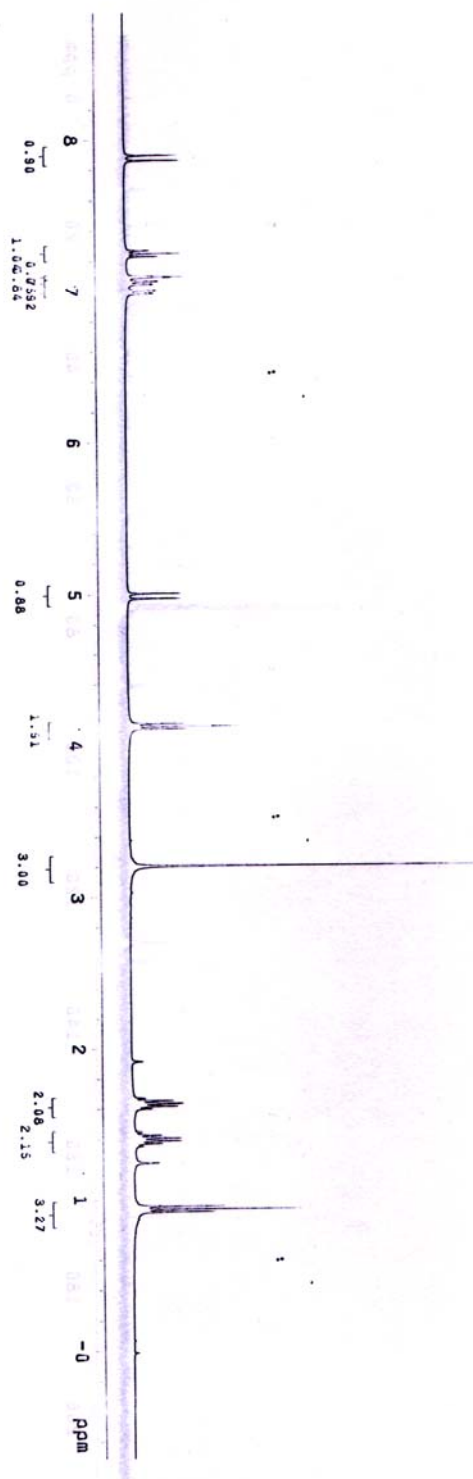
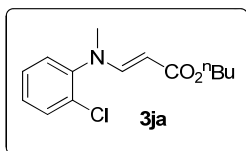


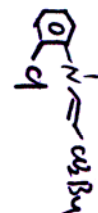
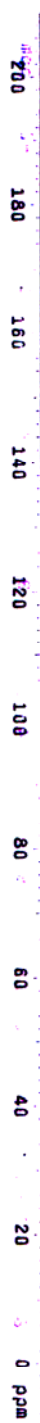
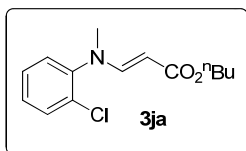












169.182

130.753
127.928

89.015

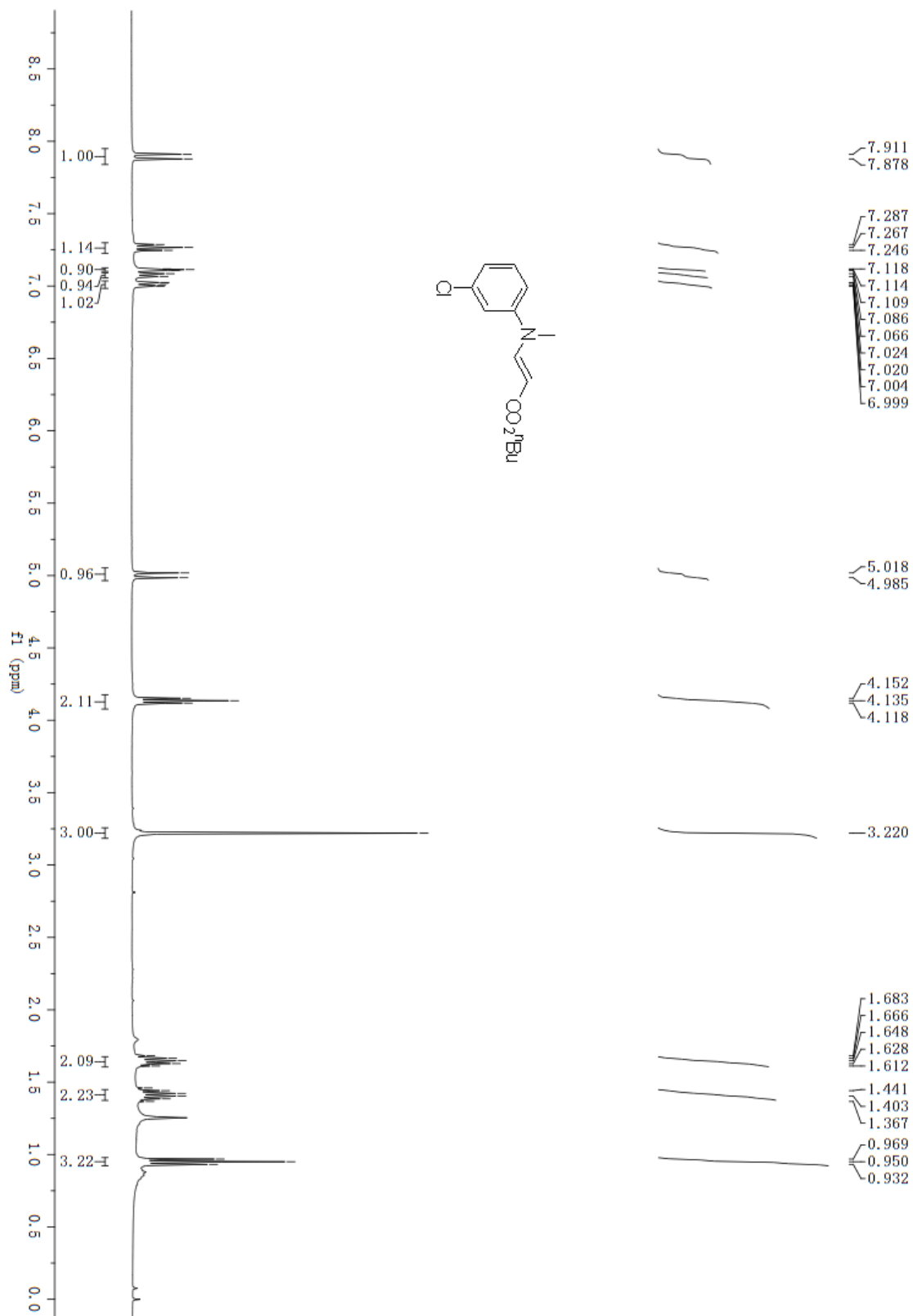
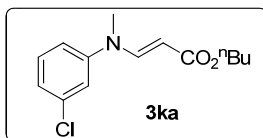
77.319
77.000
76.681

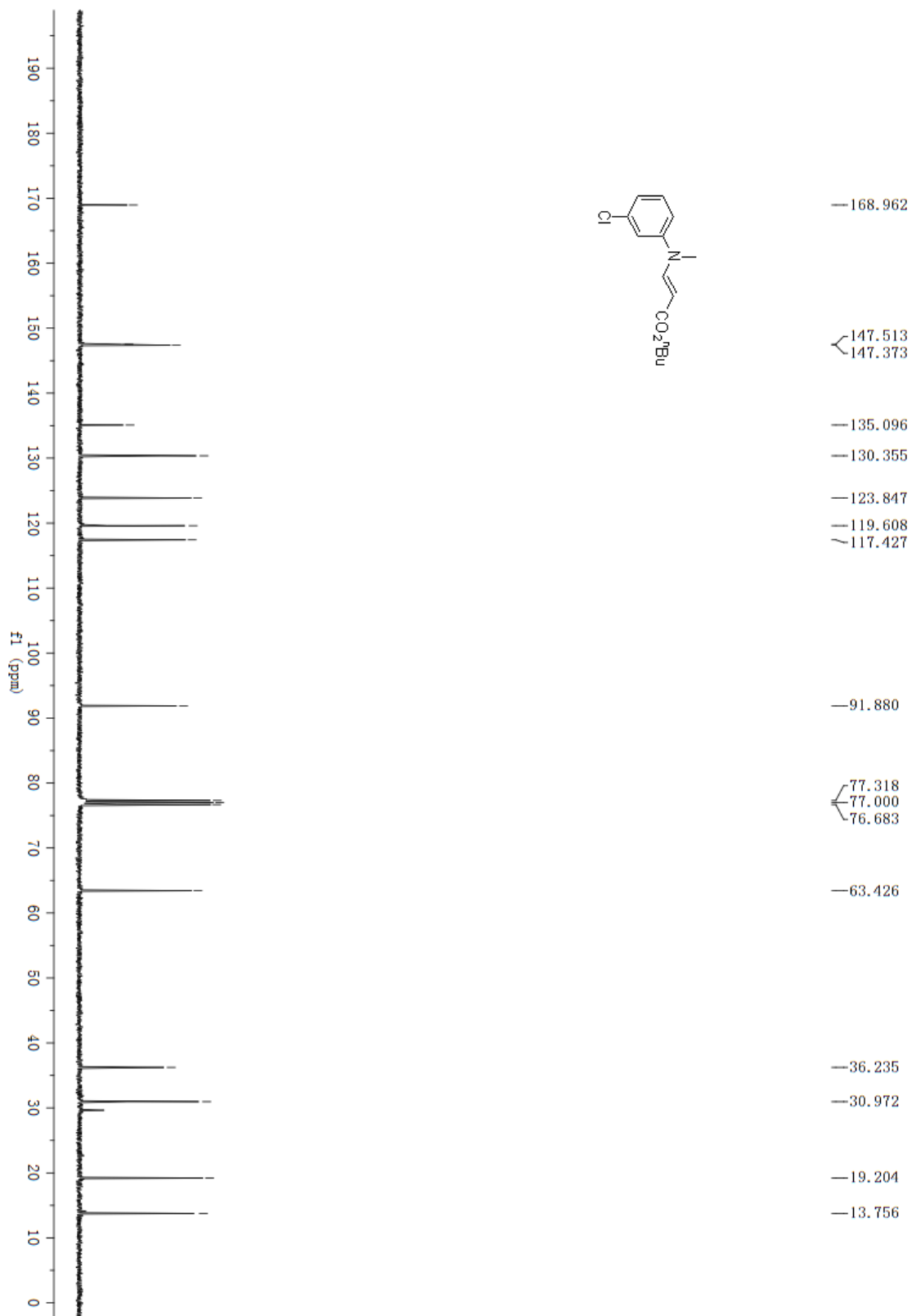
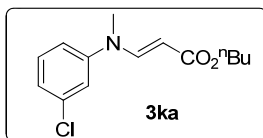
63.178

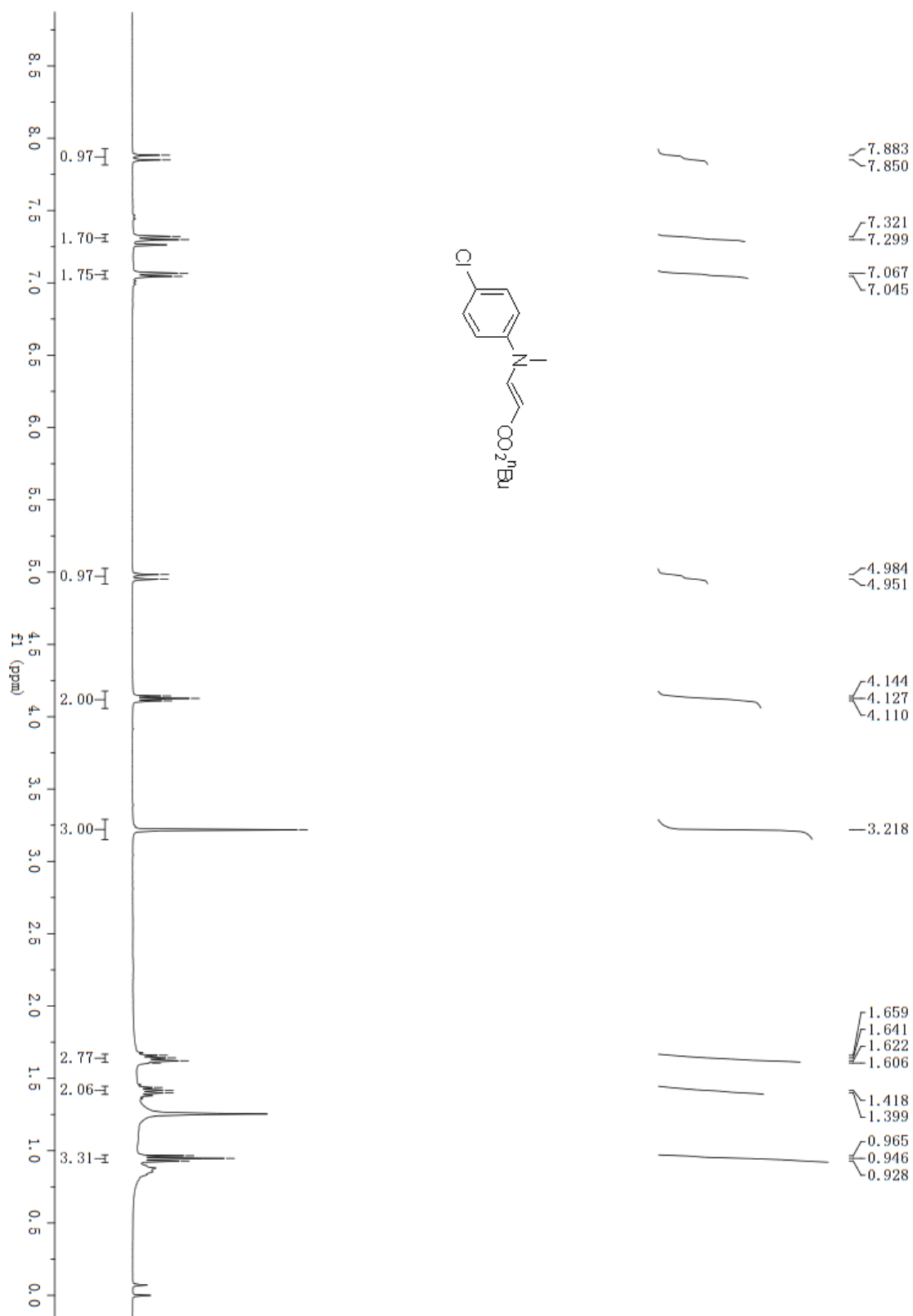
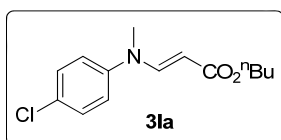
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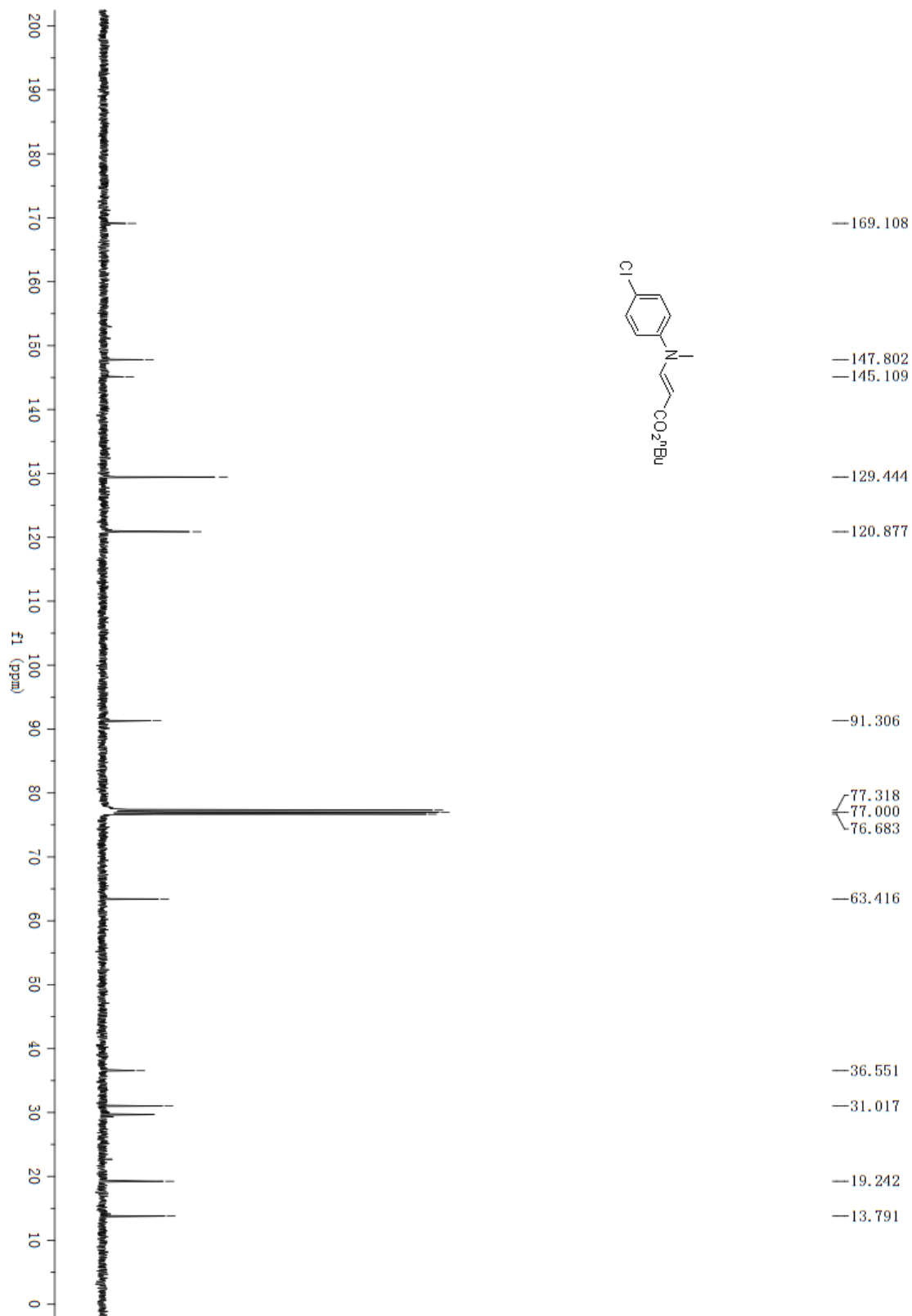
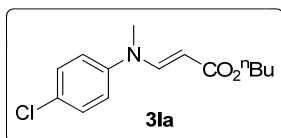
19.201

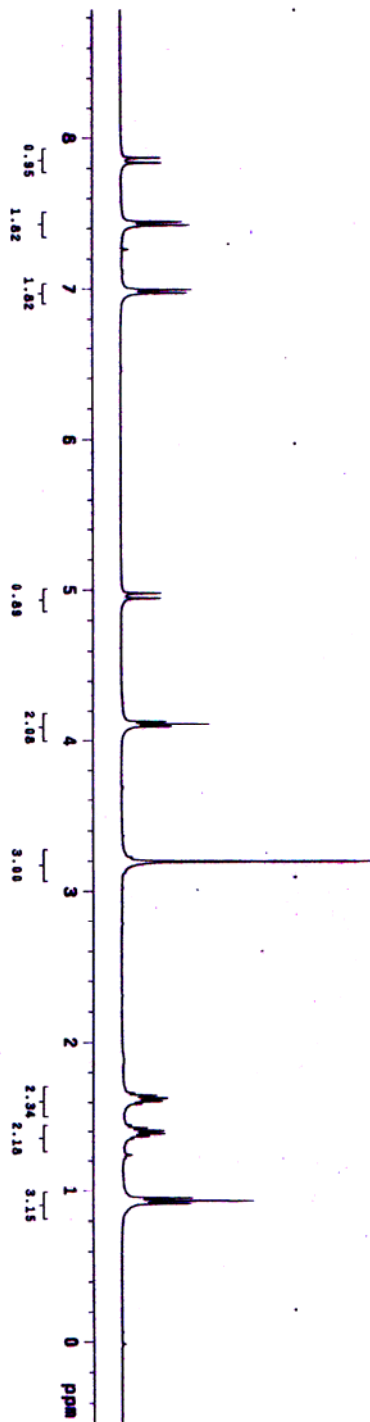
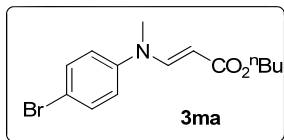
13.799

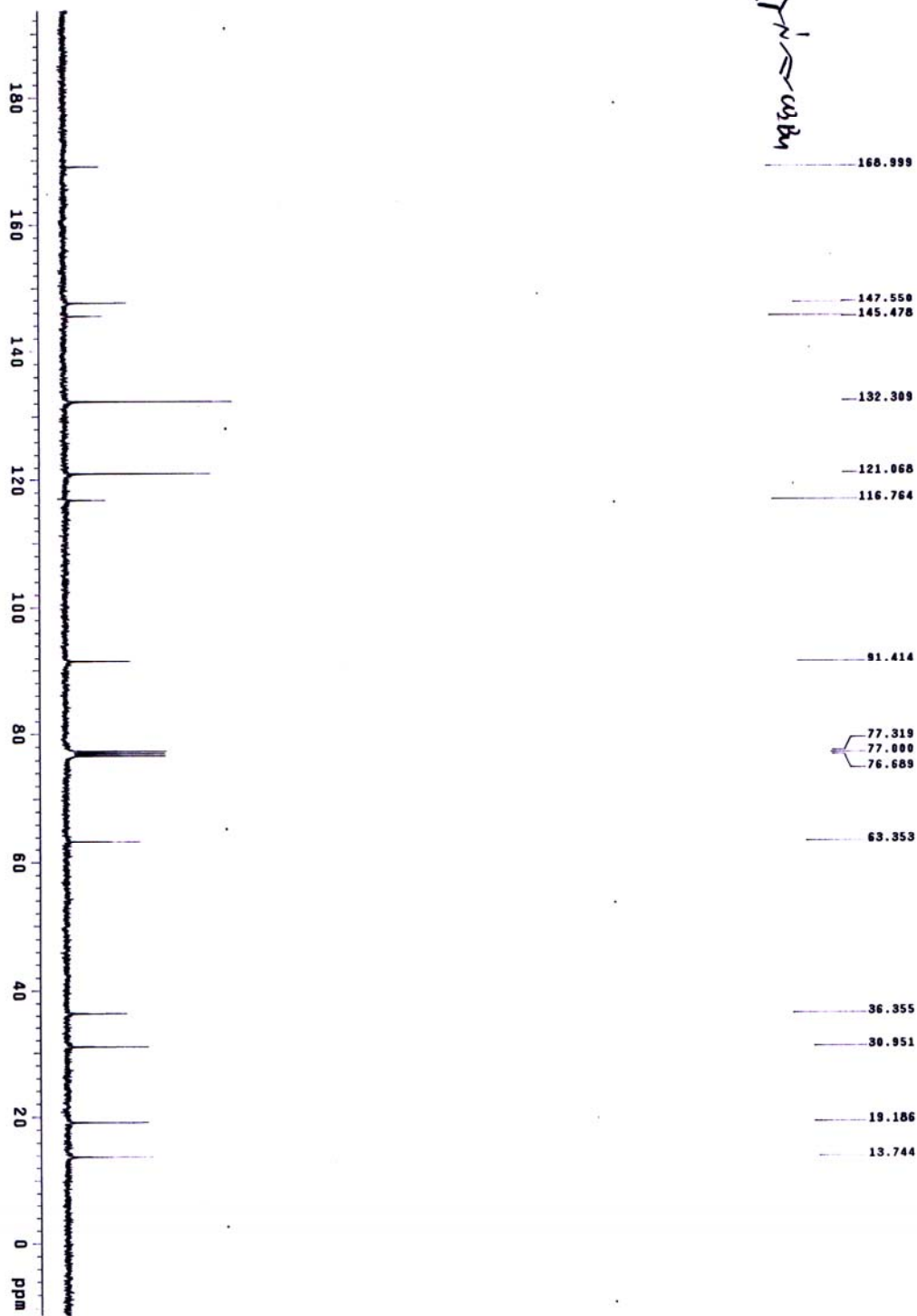
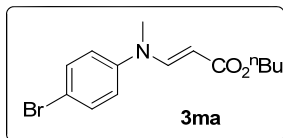


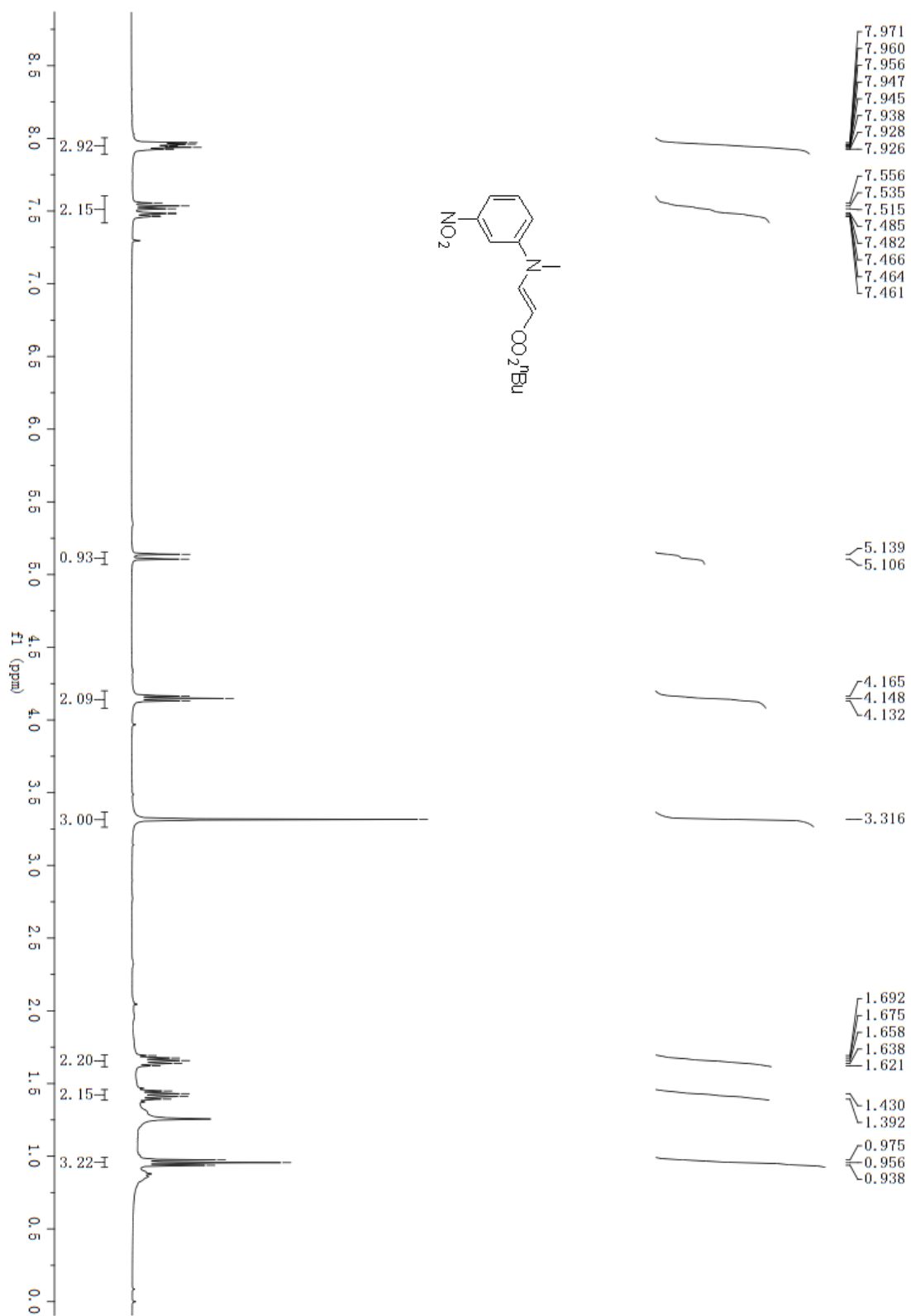
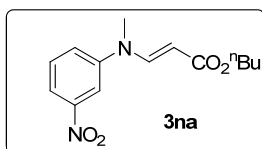


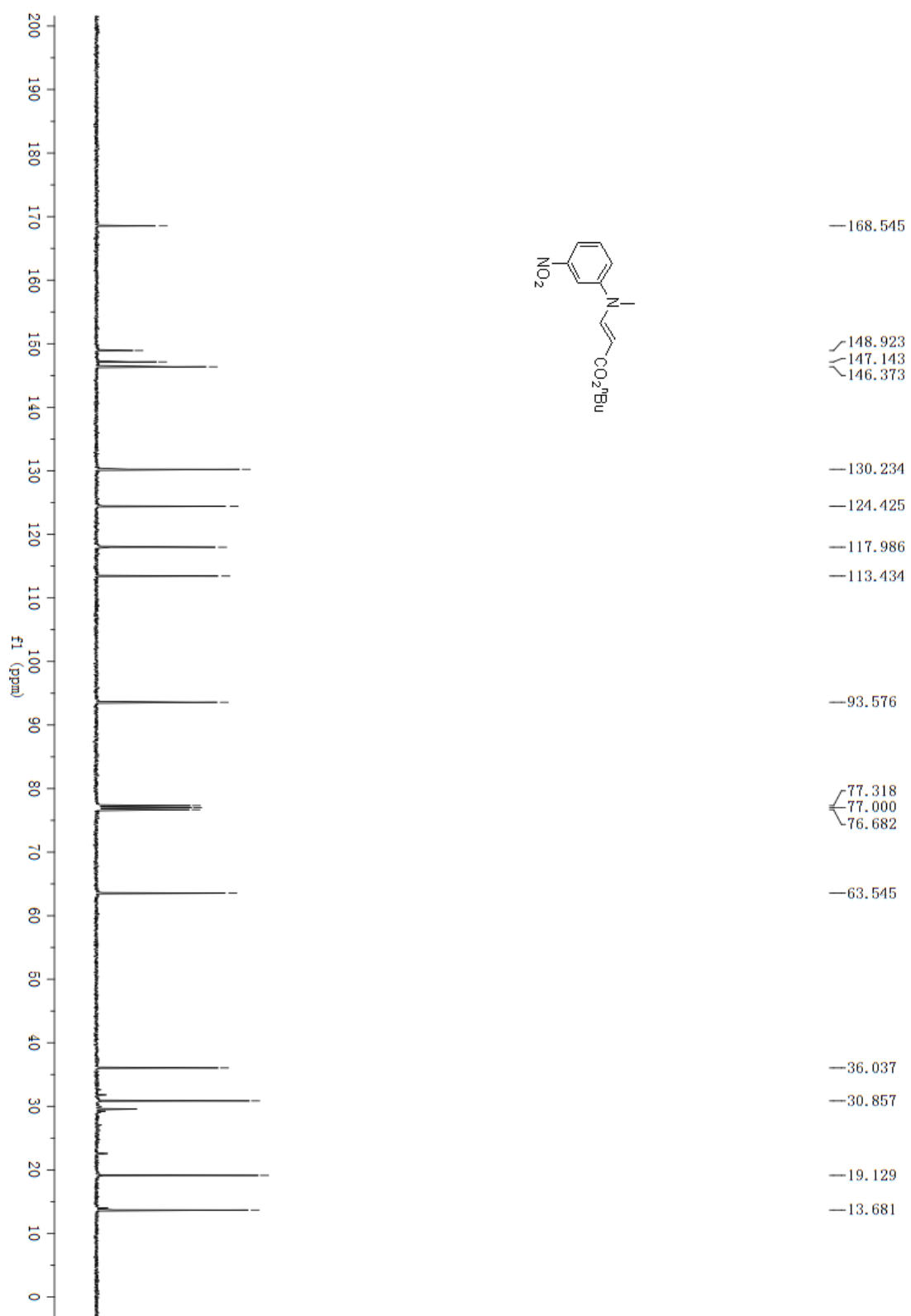
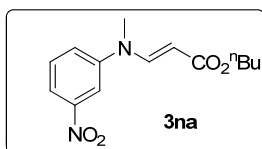


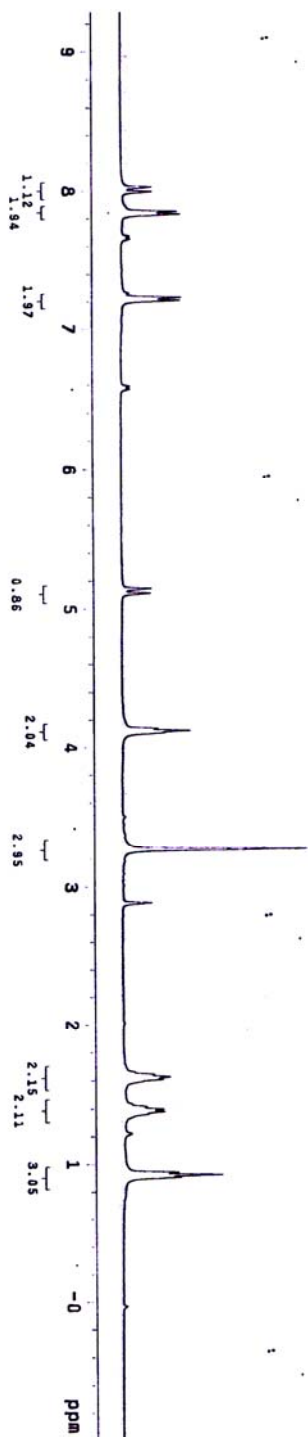
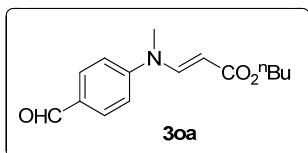


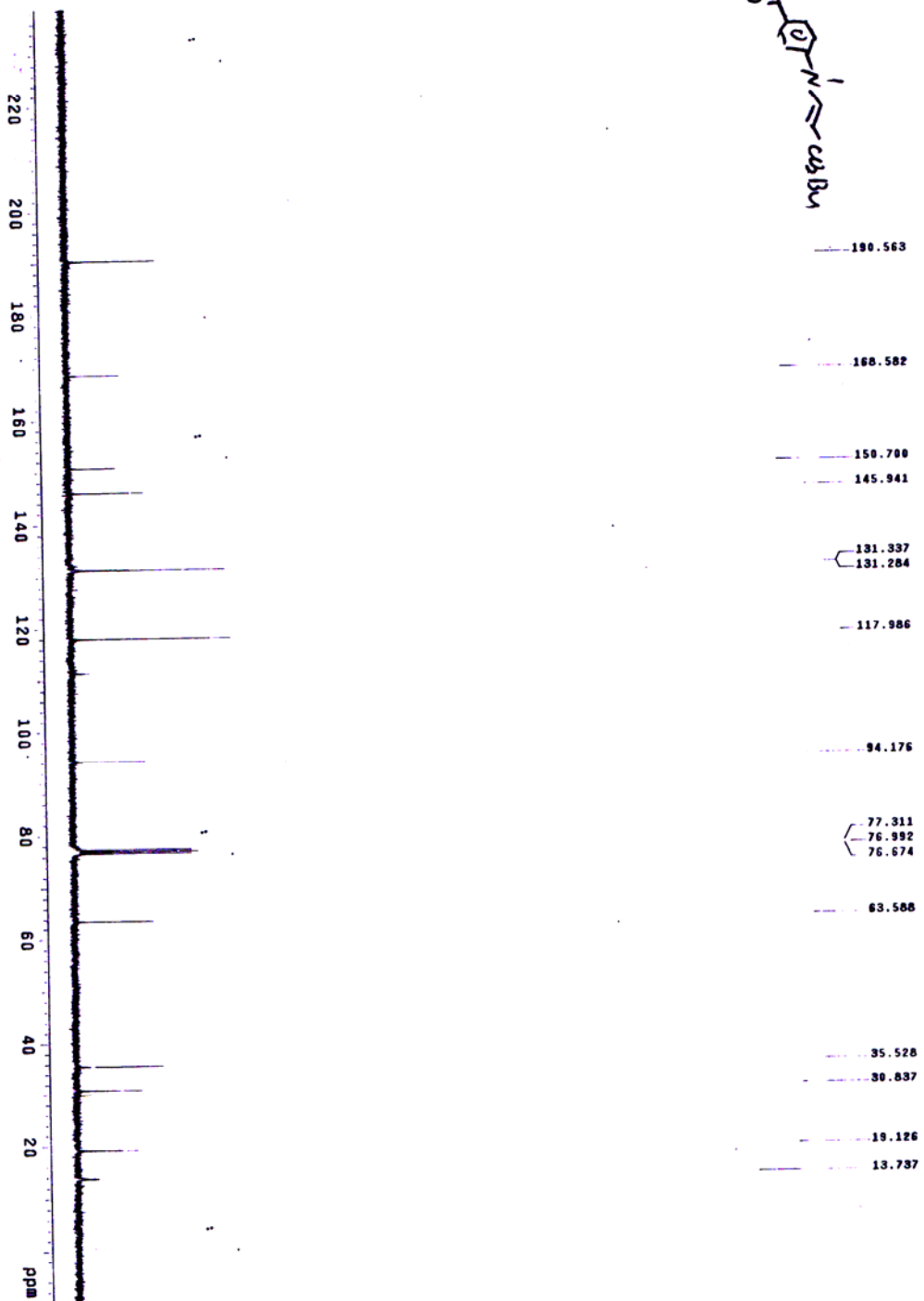
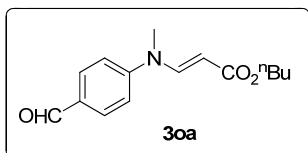


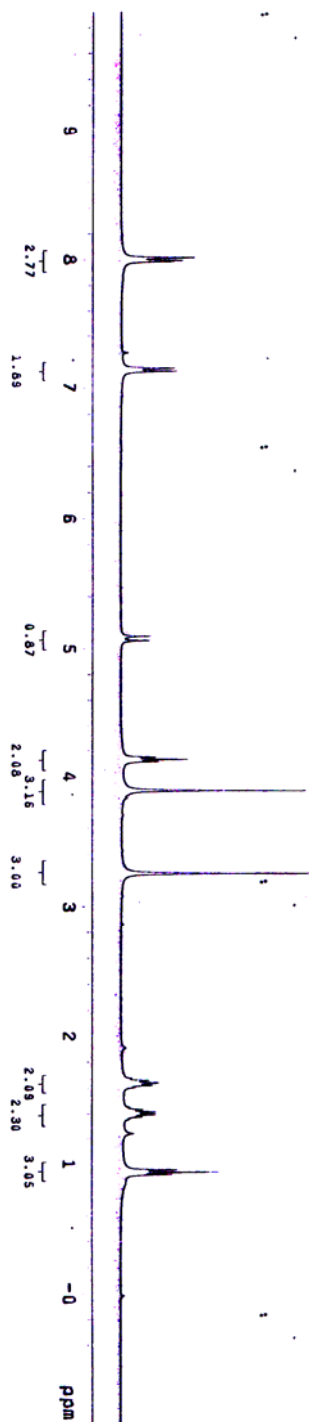
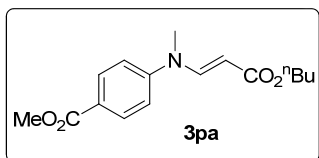












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7.987

7.153
7.132

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5.064

4.149
4.132
4.116
3.891

3.260

1.658
1.641
1.621
1.432
1.413
1.395
1.376
0.958
0.941
0.921

